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THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$ and $AsCl_3$

I. THE $SnCl_4$ - $CH_2ClCOOH$ SYSTEM

M. Usanovich, T. Sumarokova and the Student, V. Glushchenko

We have investigated the systems constituted by $HClO_4$ with CH_2COOH and its chloro derivatives [1,2,3,4,5]. Acid-base interaction has been found to exist in all of these systems, with the exception of $HClO_4$ – CCl_3COOH.

Wholly analogous results were secured earlier [6,7,8] in a study of the systems formed by H_2SO_4 with the same constituents, which thus act as oxonium bases in these systems (with the exception of CCl_3COOH).

As we were interested in learning the behavior of these bases with aprotic acids, we decided to make a systematic study of the corresponding binary systems. The aprotic acids we chose were $SnCl_4$, which is acid according to Lewis and Usanovich, and $SbCl_3$ and $AsCl_3$, which are acid only as described by Usanovich.

Of these systems the only one that has been investigated thoroughly is $SnCl_4$ – CH_3COOH [9,10]. We therefore investigated the conductance, viscosity, and density of the $SnCl_4$ – $CH_2ClCOOH$ system.

EXPERIMENTAL

The monochloracetic acid was purified by triple distillation; we collected the fraction that boiled at 182° at a pressure of 698.2 mm and sealed it into ampoules. The constants of the monochloracetic acid (m.p. 63.5°) are as follows:

d_{50} 1.3907; d_{60} 1.3777; d_{70} 1.3642; η_{50} 0.03091; η_{60} 0.02446; η_{70} 0.02051.

The stannic chloride was prepared by the direct action of chlorine upon molten metallic tin. The reaction product was freed of chlorine by boiling it for a long time with a reflux condenser and then distilling it twice. The fraction that boiled at 110° at 684 mm was collected and sealed into ampoules.

The constants of the stannic chloride were as follows:

d_{50} 2.1555; d_{60} 2.1347; d_{70} 2.1100; η_{50} 0.00683; η_{60} 0.00650; η_{70} 0.00589.

We investigated the conductance, viscosity, and density of the $SnCl_4$ – $CH_2ClCOOH$ system at 50, 60, and 70°. Our measurements of the viscosity of the $SnCl_4$ – $CH_2ClCOOH$ system are tabulated in Table 1 and shown graphically in Fig. 1. The viscosity of the system rises from $SnCl_2$ to $CH_2ClCOOH$, passing through a maximum in the vicinity of monochloracetic acid. As the temperature is raised, the position of the maximum shifts toward the more viscous constituent, $CH_2ClCOOH$, in accordance with the general concept of N.S.Kurnakov.

It is worthy of note that as the temperature rises, the viscosity drops faster in the vicinity of the maximum than does the viscosity of $CH_2ClCOOH$; that is why this maximum is less pronounced in the 70° isotherm. It is evident that the maximum would vanish at still higher temperatures. The course of the

TABLE 1

Mol.% $SnCl_4$	$\eta \times 10^3$		
	50°	60°	70°
100.00	6.83	6.50	5.89
77.08	8.36	7.64	6.80
66.63	9.48	8.74	7.77
49.28	14.10	13.21	11.21
34.56	20.03	17.96	14.50
25.11	29.27	23.15	18.42
20.41	39.21	27.41	19.85
14.91	41.70	30.13	22.14
9.57	41.00	-	22.82
9.51	41.93	30.69	23.35
5.06	39.44	31.15	24.41
2.50	33.05	26.15	21.00
0.00	30.91	24.46	20.51

TABLE 2

Mol.% $SnCl_4$	$\kappa \times 10^4$		
	50°	60°	70°
58.52	0.098	-	0.090
49.25	0.290	-	0.280
39.95	0.970	0.830	0.720
38.52	1.248	1.225	1.179
36.37	1.626	1.554	1.484
36.14	1.368	1.439	1.530
31.72	1.992	1.956	1.872
30.46	2.131	1.953	1.735
25.11	3.019	2.693	-
20.41	3.549	3.656	-
18.55	-	4.523	-
14.91	4.125	-	-
13.65	4.179	4.761	5.087
9.57	-	4.892	-
9.51	4.234	4.648	4.877
7.85	4.092	4.547	4.815
5.06	2.621	-	-
2.50	1.560	1.767	1.916

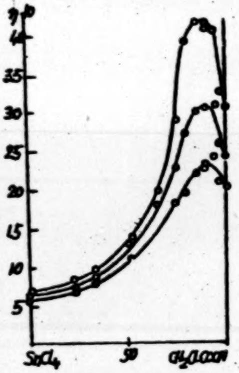

Fig. 1.

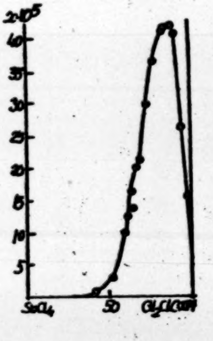

Fig. 2.

viscosity isotherms is evidence of the presence of chemical interaction between the constituents.

The viscosity of our system differs considerably from that of the $SnCl_4$ – CH_3COOH system, in which the viscosity rose very much when the constituents were mixed together [9,10], while the maximum did not shift, corresponding to a 3;1 stoichiometric ratio of CH_3COOH to $SnCl_4$.

Our measurements of conductance are listed in Table 2. The isotherms of specific conductance are complicated. They exhibit a double bend at 33 mol.% of $SnCl_4$ and a maximum at 10-12 mol.% of $SnCl_4$. The conductance diagram, plotted from the data in Table 2, is reproduced in Fig. 2. Since the temperature coefficient of the conductance is very small, we reproduce only one isotherm in the diagram, that for 50°.

Inspection of the figures in Table 2 indicates that the temperature coefficient of conductance changes sign at 20 mol.% $SnCl_4$; up to a concentration of 20 mol.% $SnCl_4$ the conductance rises with the temperature, while above that concentration the conductance drops as the temperature is raised. Hence, the isotherms intersect at a single point – 20 mol.% of $SnCl_4$. We dispensed with the calculation of the temperature coefficient owing to the negligible change of conductance with temperature.

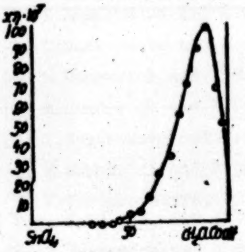

Fig. 3.

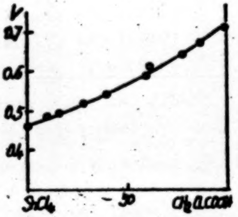

Fig. 4.

TABLE 3

Mol. % $SnCl_4$	$\varkappa\eta \times 10^7$ 50°
75.0	0.17
70.0	0.38
65.0	0.61
60.0	0.81
55.0	1.75
50.0	3.30
45.0	6.00
40.0	12.54
35.0	24.65
30.0	34.23
25.0	55.50
20.0	71.00
15.0	89.38
10.0	99.96
5.0	62.92
2.5	51.58

TABLE 4

Per cent $SnCl_4$		d		
Molar	Weight	50°	60°	70°
100.0	100.00	2.1555	2.1347	2.1100
77.08	90.33	2.0631	2.0418	2.0190
66.63	84.62	2.0204	1.9998	1.9747
49.28	72.81	1.9128	1.8980	1.8767
34.56	60.66	1.8228	1.8009	1.7775
18.51	40.97	1.6855	1.6675	1.6555
14.91	39.08	1.6184	1.6014	1.5858
9.57	22.49	1.5513	1.5346	1.5186
5.06	12.81	1.4774	1.4624	1.4499
0.00	0.00	1.3907	1.3777	1.3642

To eliminate the influence of viscosity, we corrected the specific conductance for viscosity (Table 3). Figure 3 shows the 50 ° isotherms of the corrected conductance. As we see in Fig. 3, applying this correction simplifies the shape of the conductance isotherm. It exhibits a maximum at ~10 mol.% $SnCl_4$. The maximum of the corrected conductance does not occur at a rational ratio of the constituents.

The density measurements are listed in Table 4.

Figure 4, which plots the specific volume as a function of the concentration (in per cent by weight), shows that shrinkage occurs in the system.

Thus, our data indicate that the system constituents interact. We secured no definite indications of the compositions of the compounds formed.

SUMMARY

1. The conductance, viscosity, and density of the $SnCl_4$ - $CH_2ClCOOH$ system have been investigated at 50, 60, and 70°.

2. The existence of a maximum on the viscosity and conductance isotherms is evidence of chemical interaction between the constituents.

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THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$ and $AsCl_3$

II. THE $SnCl_4$ - CCl_3COOH and $SnCl_4$ - $CHCl_2COOH$ SYSTEMS

T. Sumarokova and M. Usanovich

Investigation of the $SnCl_4$ – $CH_2ClCOOH$ system [1] has shown that the constituents of that system interact chemically and that $CH_2ClCOOH$ acts as an oxonium base with respect to $SnCl_4$. As we have stated before, protogenic acids, including the strongest acid known, $HClO_4$, cannot make CCl_3COOH act as a base [2,3]. We therefore decided to continue our systematic investigations, making a study of the systems $SnCl_4$ – CCl_3COOH and $SnCl_4$ – $CHCl_2COOH$.

EXPERIMENTAL

The trichloracetic acid was purified by triple distillation; the fraction that distilled at 190° and 685.5 mm was collected and fractionated into ampoules. The resulting acid had the following constants: d_{50} 1.6156; η_{50} 0.04824.

The dichloracetic acid was double distilled, the fraction that boiled at 187° and 682 mm being collected. The constants of the resultant acid were: d_{35} 1.5302; η_{35} 0.04779.

The stannic chloride was prepared as described previously.

The $SnCl_4$ – CCl_3COOH and $SnCl_4$ – $CHCl_2COOH$ systems proved to be nonconductors; we investigated their viscosity and density. The $SnCl_4$ – CCl_3COOH system was investigated at 50, 60, and 75°; while the $SnCl_4$ – $CHCl_2COOH$ system was investigated at 35, 50, 60, and 70°.

The data on the viscosity of the $SnCl_4$ – CCl_3COOH system are listed in Table 1 and plotted in Fig. 1. The viscosity of this system rises uninterruptedly from $SnCl_4$ to CCl_3COOH. The viscosity isotherm is concave upward, as the temperature is raised, the viscosity drops considerably in the vicinity of the CCl_3COOH.

TABLE 1

Mol. % $SnCl_4$	$\eta \times 10^3$		
	50°	60°	70°
100.00	6.83	6.50	5.89
66.70	9.59	8.67	7.57
43.95	14.48	12.83	11.34
19.11	26.60	22.44	19.21
0.00	48.24	38.15	30.33

TABLE 2

Percent $SnCl_4$		d		
Molar	Weight	50°	60°	70°
100.00	100.00	2.1555	2.1347	2.1100
66.70	75.34	1.9875	1.9648	1.9440
43.95	55.44	1.8749	1.8552	1.8397
19.11	27.35	1.7336	1.7117	1.7012
0.00	0.00	1.6156	1.5970	1.5804

The results of our determinations of density in the $SnCl_4$ – CCl_3COOH system are given in Table 2.

No changes occur in this system, as is seen in Fig. 2, in which the specific volume as a function of the composition (in per cent by weight) is plotted as an additive straight line.

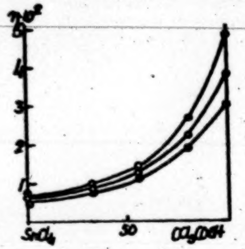

Fig. 1.

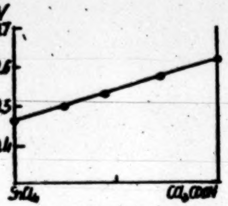

Fig. 2.

The data on the viscosity of the $SnCl_4$ – $CHCl_2COOH$ system are listed in Table 3. The viscosity is plotted in Fig. 3 as a function of the composition.

TABLE 3

Mol. % $SnCl_4$	η x 10^3 35°	50°	60°	70°
100.00	–	6.83	6.50	5.89
80.50	8.31	7.05	6.27	5.77
50.02	14.45	10.90	9.69	8.64
32.11	21.21	16.30	14.61	13.24
20.27	26.21	19.82	16.91	14.05
10.00	36.57	26.09	21.58	18.16
0.00	47.79	32.43	26.26	21.46

The viscosity isotherms of the $SnCl_4$ – $CHCl_2COOH$ system are concave upward. The viscosity drops faster with rising temperature in the region adjacent to the $CHCl_2COOH$; as a result the isotherms for the lower temperatures exhibit a greater sag than those for the higher ones.

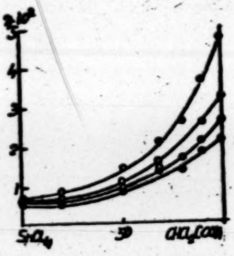

Fig. 3.

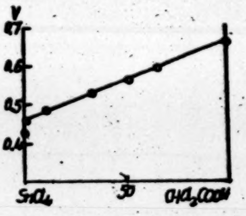

Fig. 4.

The data on the density of the system are given in Table 4.

The variation of the specific volume with the composition (in per cent by weight) is plotted in Fig. 4. As we see, the variation of specific volume with the composition obeys the law of mixtures, that is, it is a straight line.

The absence of any conductivity, the monotonous course of the viscosity isotherms, and the absence of any change in volume when the constituents of the systems $SnCl_4$ – CCl_3COOH and $SnCl_4$ – $CHCl_2COOH$ are mixed together indicate that the constituents of these systems do not interact with each other.

TABLE 4

Per cent $SnCl_4$		d			
Molar	Weight	35°	50°	60°	70°
100.00	100.00	–	2.1555	2.1347	2.1100
80.50	89.55	2.0936	2.0562	2.0386	2.0206
50.02	66.90	1.9239	1.8898	1.8776	1.8612
32.11	48.86	1.8072	1.7803	1.7660	1.7484
20.27	33.96	1.7164	1.6904	1.6779	1.6650
0.00	0.00	1.5302	1.5106	1.4985	1.4868

SUMMARY

1. The viscosity and density of the system $SnCl_4 - CCl_3COOH$ have been investigated at 50, 60, and 70°.

2. The viscosity and density of the system $SnCl_4 - CHCl_2COOH$ have been investigated at 35, 50, 60, and 70°.

3. The measurements of viscosity and density and the absence of any conductivity in the $SnCl_4 - CCl_3COOH$ and $SnCl_4 - CHCl_2COOH$ systems are proof that there is no chemical interaction present in these systems.

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*See CB translation p. 1075 ff.

THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$ and $AsCl_3$

III. THE $SbCl_3$ - CH_3COOH SYSTEM

M. Usanovich and T. Sumarokova

Investigation of the systems constituted by $SnCl_4$ with CH_3COOH [1], $CH_2ClCOOH$ [2], $CHCl_2COOH$ and CCl_3COOH [3] has shown that $SnCl_4$ behaves like an acid toward CH_3COOH and $CH_2ClCOOH$, forcing them to act as oxonium bases, though it does not interact with $CHCl_2COOH$. In this respect, $SnCl_4$ differs from the strong hydrogen acids H_2SO_4 and $HClO_4$, which cause $CHCl_2COOH$ to act as a base as well, [4,5].

We were interested in studying the behavior of acetic acid and of its chloro derivatives toward $SbCl_3$, which is an acid as we see it, but not according to Lewis.

We began our investigation of this series of systems with the system $SbCl_3$ - CH_3COOH, the fusibility of which had previously been investigated by B.N.Menshutkin [6].

EXPERIMENTAL

The acetic acid was desiccated with calcined $CuSO_4$, distilled, fractionally frozen, and sealed into ampoules. This acid had a m.p. of 165°.

We investigated the conductance, viscosity, and density of the $SbCl_3$ - CH_3COOH system at 20, 50, and 60°.

The viscosity figures are tabulated in Table 1. Figure 1 shows the viscosity as a function of the composition. The viscosity isotherms exhibit a maximum located at 52-53 mol.% of $SbCl_3$. The viscosity maximum shifts toward the $SbCl_3$ end as the temperature is raised. The presence of a maximum on the viscosity isotherms is evidence of chemical interaction between the components and of the formation of a compound with the composition of $SbCl_3 \cdot CH_3COOH$.

The figures for the specific conductance are listed in Table 2.

The data in Table 2 have been used to plot the curve showing the variation of the specific conductance with composition, reproduced in Fig. 2. As we see, the specific conductance of CH_3COOH increases as $SbCl_3$ is added to it, reaching a maximum value and then dropping fairly rapidly. The conductance maximum is located at 70-80 mol.% $SbCl_3$. As the temperature is raised, the conductance rises, and the maximum is shifted toward the CH_3COOH end. When the conductance is corrected for viscosity, the corrected conductance repeats the qualitative shape of the specific conductance curve, passing through a maximum that corresponds to the compound $2SbCl_3 \cdot CH_3COOH$ and does not shift as the temperature is changed (Fig. 3).

The data on the corrected conductance are listed in Table 3.

We computed the temperature coefficient of conductance from the smooth curve of the specific conductance, the value of the coefficient varying from 2.5 to 6.2%.

TABLE 1

Mol. % $SbCl_3$	$\eta \times 10^2$		
	20°	50°	60°
100.00	Cryst.	3.93	3.15
91.18	Cryst.	4.30	-
84.23	Cryst.	4.77	3.60
79.90	19.13	5.44	4.68
74.06	-	5.70	-
71.23	23.98	5.77	4.35
68.75	24.73	5.85	4.18
60.21	28.03	6.28	4.41
53.94	29.95	6.32	4.39
52.22	29.17	6.28	4.22
51.32	26.76	5.88	4.16
44.09	23.26	4.83	3.86
38.39	13.18	4.01	2.95
23.07	28.60	2.84	-
11.92	3.57	-	-

TABLE 2

Mol. % $SbCl_3$	$\kappa \times 10^4$		
	20°	50°	60°
91.18	-	33.56	37.44
84.23	-	51.64	59.40
79.90	26.33	61.28	-
74.06	-	57.23	-
68.75	22.42	60.40	69.11
60.21	19.26	52.14	63.86
53.94	15.37	45.61	56.85
52.22	14.69	-	-
51.32	14.34	42.72	53.70
44.09	11.11	28.90	38.64
38.39	6.80	17.23	21.29
23.07	5.47	-	-
11.92	1.92	4.23	5.21

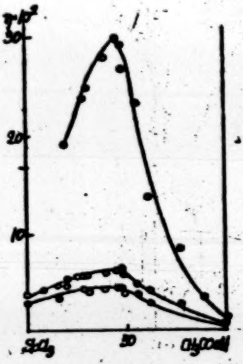

Fig. 1.

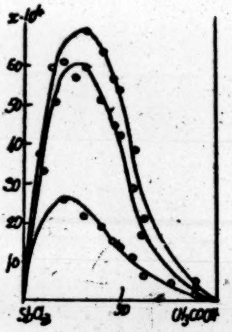

Fig. 2.

The values of the temperature coefficient are tabulated in Table 4, while the variation of the temperature coefficient of conductance with composition is plotted in Fig. 4.

We see from Table 4 and Fig. 4 that the temperature coefficient of conductance exhibits a maximum at a constituent ratio that corresponds to the compound $SbCl_3 \cdot CH_3COOH$.

Thus, our data on conductance and viscosity indicate the presence of acid-base interaction, resulting in the formation of the compound $SbCl_3 \cdot CH_3COOH$, and of the compound $2SbCl_3 \cdot CH_3COOH$. Menshutkin [2] discovered an equimolecular compound with a m.p. of 19° in his fusibility research. We believe its structure

TABLE 3

Mol. % $SbCl_3$	$\kappa\eta \times 10^5$
	50°
91.18	14.43
84.23	24.27
79.90	33.34
68.75	35.33
60.21	32.74
53.94	30.25
51.32	25.12
44.09	13.96
38.39	6.91
23.07	2.69
11.92	0.60

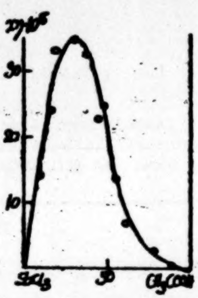

Fig. 3.

TABLE 4

Mol. % $SbCl_3$	α in per cent, at 20-25°
90.0	2.5
80.0	3.66
70.0	5.17
60.0	6.09
50.0	6.17
40.0	4.57
30.0	3.05
20.0	2.40

TABLE 5

Per cent $SbCl_3$		d		
Molar	Weight	20°	50°	60°
100.00	100.00	Cryst.	2.7352	2.7148
91.18	97.40	Cryst.	2.6391	-
84.23	95.28	Cryst.	2.5667	2.5418
79.90	93.79	2.5824	2.5174	2.4912
74.06	91.52	-	2.4644	2.4445
71.23	90.36	2.4712	2.4026	2.3831
68.75	89.32	2.4356	2.3741	2.3468
52.22	80.64	2.1756	2.1176	2.1004
51.32	80.04	2.1632	2.1050	2.1014
44.09	75.00	2.0353	1.9833	1.9686
23.07	53.21	1.5769	1.5693	-
11.92	34.75	1.3400	-	-

to be as follows:

$[SbCl_2 \cdot CH_3COOH]^+ \cdot Cl^-$.

We are inclined to assign the structure of $[SbCl_2 \cdot CH_3COOH]^+ SbCl_4^-$ to the other compound, which exists, apparently, only in the liquid phase.

The density data are tablulated in Table 5.

The specific volume is plotted as a function of the composition in Fig. 5. As we see, a slight shrinkage occurs in the system when the constituents are mixed together.

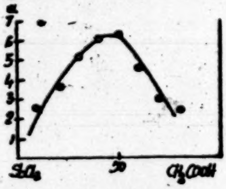

Fig. 4.

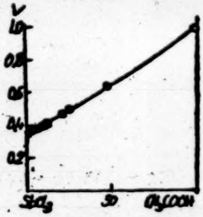

Fig. 5.

SUMMARY

1. A study has been made of the conductance, viscosity, and density of the $SbCl_3 - CH_3COOH$ system at 20, 50, and 60°.

2. The diagrams of the viscosity, the corrected conductance, and the temperature coefficient of conductance indicate the presence of the compounds $SbCl_3 \cdot CH_3COOH$ and $2SbCl_3 \cdot CH_3COOH$. The compound $SbCl_3 \cdot CH_3COOH$ had been produced previously by B.N.Menshutkin.

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*See CB translation p. 1075 ff.

**See CB translation p. 1083 ff.

THE REACTION OF UREA WITH DIATOMIC PHENOLS

THE TERNARY SYSTEM UREA-RESORCINOL-HYDROQUINONE

D. E. Dionisyev and N. Z. Rudenko

Not much has been written in the literature [1] on the reaction of urea with diatomic phenols, although it is definitely interesting.

We have investigated the interactions in a ternary system, consisting of urea, resorcinol, and hydroquinone.

PROCEDURE

The investigation was made by the visual polythermal method of physico-chemical analysis, which makes it possible to detect chemical interaction between the components in the "composition-property" diagrams without having to isolate the resulting compounds preparatively. We recorded the temperature at which the first crystals appeared as the molten mixture solidified, and the temperature at which the last crystals vanished when the mixture was melted. The coincidence of these two temperatures indicated that equilibrium was attained from both ends [2]. In the few instances when the temperature at which the first crystals appeared was lower than the temperature at which the last crystals disappeared, owing to supercooling of the system in spite of vigorous stirring and the use of primers, we took the temperature at which the last crystals vanished as our basis.

The substance was placed in a test tube fitted with a thermometer and a stirrer. The test tube was placed in a glass sleeve to ensure more uniform heating and cooling. The melting point was determined in a capillary attached to a thermometer, which was air-jacketed to provide even heating and to eliminate the effects of convection currents. The initial substances used bore the label "pure"; after they had been recrystallized from water their melting points were quite close to those given in the reference works [3]: 133° for urea, 110° for resorcinol, and 171° for hydroquinone.

It should be noted that we did not observe any decomposition of the urea, with the evolution of ammonia, at temperatures close to its melting point [4].

EXPERIMENTAL

BINARY SYSTEMS

The Urea-Resorcinol System

The urea – resorcinol system has been investigated by Pushin and Rikovsky [1]; we repeated their investigation.

The results are set forth in Table 1 and in Fig. 1. As we see, urea and resorcinol form a clearly apparent compound, $CO(NH_2)_2 \cdot C_6H_4(OH)_2$, with a m.p. of 103.5° and a urea:resorcinol ratio of 1:1, and exhibit two eutectic points: the first eutectic E_1 at 74 mol.% of urea, with a m.p. of 86.5°, and the second, E_2, at 22.5 mol.% of urea, with a m.p. of 84.8°.

TABLE 1

No.	Mol.% urea	M.p., °C	No.	Mol.% urea	M.p., °C
1	100	133	12	45	101
2	90	122.5	13	40	99.4
3	80	115	14	30	91
4	75	88	15	25	87
5	74	86.5	16	24	86
6	73	87.5	17	22.5	84.8
7	72	89	18	21	86.1
8	70	92.8	19	20	88.6
9	60	99	20	15	95
10	55	101.5	21	10	101
11	50	103.5	22	0	110

TABLE 2

No.	Mol.% urea	M.p., °C	No.	Mol.% urea	M.p., °C
1	100	133	13	55	127.5
2	90	122.1	14	50	129.2
3	85	116.5	15	45	128
4	82.5	114	16	42	127
5	80	111.3	17	41	126.4
6	79	110.5	18	40	127.1
7	78	111	19	37.5	130
8	77.5	112.6	20	35	134.3
9	75	115	21	30	140.1
10	70	120	22	20	151
11	65	122.7	23	10	161.3
12	60	126	24	0	171

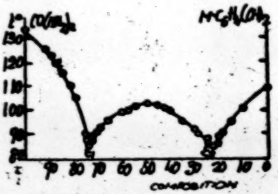

Fig. 1.

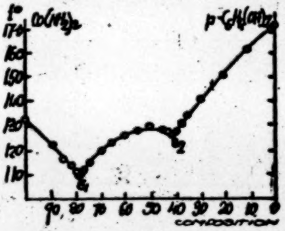

Fig. 2.

The Urea - Hydroquinone System

This system was likewise studied by Pushin and Rikovsky, and we repeated their investigation [1].

The research results set forth in Table 2 and Fig. 2, indicate that urea and hydroquinone also form a compound $CO(NH_2)_2 \cdot C_6H_4(OH)_2$ with a m.p. of 129.2°, containing 50 mol.% of urea and 50 mol.% of hydroquinone. The eutectics are: E_1 at 79 mol.% of urea, with a m.p. of 110.5°, and E_2 at 41 mol.% of urea, which is not so low, with a m.p. of 126.4°.

The Hydroquinone - Resorcinol System

The hydroquinone - resorcinol system illustrated in Table 3 and Fig. 3 was previously investigated by Jaeger [5] and Senden [6]; we repeated their researches, by and large confirming their results. This system exhibits a single eutectic at 70 mol.% of resorcinol, with a m.p. of 88° instead of the 86° given by the authors cited.

SECTIONS

We investigated 17 sections in order to plot the crystallization surface of this ternary system.

Urea - 50 mol.% resorcinol and 50 mol.% hydroquinone section. The results

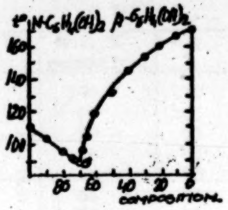

Fig. 3.

TABLE 3

No.	Mol.% resorcinol	M.p.,	No.	Mol.% resorcinol	M.p., °
1	100	110	9	60	120
2	90	90	10	50	134
3	80	97	11	40	145
4	75	91	12	30	150
5	72.5	89.7	13	20	158
6	70	88	14	10	167
7	67.5	97	15	0	171
8	65	105			

of our research (Table 4, Fig. 4) indicate that the diagram consists of four crystallization branches: Aa_1 for urea; a_1a_2 for the compound $CO(NH_2)_2 \cdot p\text{-}C_6H_4(OH)_2$, a_2a_3 for the compound $2CO(NH_2)_2 \cdot p\text{-}C_6H_4(OH)_2 \cdot m\text{-}C_6H_4(OH)_2$ (Fig. 21); and Ba_3 for hydroquinone.

The points at which the branches intersect are: a_1 at 70 mol.% urea, with a m.p. of 100 °; a_2 at 60 mol.% of urea, with a m.p. of 105°; and a_3 at 35 mol.% of urea, with a m.p. of 97°.

TABLE 4

No.	Mol.% urea	M.p., °	No.	Mol.% urea	M.p., °
1	100	133	15	57.5	107
2	90	125	16	55	108
3	80	116	17	52.5	108.5
4	75	110	18	50	109
5	72.5	106.5	19	47.5	107
6	71	102	20	45	105
7	70	100	21	40	102
8	69	101	22	36	98
9	67.5	102.5	23	35	97
10	65	104	24	34	103
11	62.5	100.5	25	30	112
12	61	105	26	20	122
13	60	105	27	10	129
14	59.0	106	28	0	134

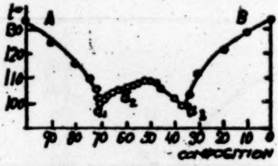

Fig. 4. Section: urea – 50 mol.% resorcinol and 50 mol.% hydroquinone.

In the rest of the sections we confined ourselves to determing the composition and the temperature of the points at which the branches meet, for they are similar, in one way or another, to the ones discussed above, and are apparent from the respective tables and figures.

Section: resorcinol – 50 mol.% urea and 50 mol.% hydroquinone (Table 5, Fig. 5). a_1 at 60 mol.% resorcinol, with a m.p. of 70°; a_2 at 8 mol % resorcinol, with a m.p. of 117°.

Section: hydroquinone – 50 mol.% urea and 50 mol.% resorcinol (Table 6, Fig. 6). a_1 at 30 mol.% hydroquinone, with a m.p. of 95°; a_2 at 20 mol.% hydroquinone, with a m.p. of 83°.

Section: urea – 80 mol.% hydroquinone and 20 mol.% resorcinol (Table 7, Fig. 7). a_1 at 77 mol.% urea, with a m.p. of 109°; a_2 at 46 mol.% urea, with a m.p. of 113°.

TABLE 5

No.	Mol. % resorcinol	M.p., °
1	100	110
2	90	103
3	80	99
4	70	88
5	65	78
6	61	71
7	60	70
8	59	71
9	55	77
10	50	89
11	40	98
12	30	109
13	20	115
14	10	116
15	9	117
16	8	117
17	7	118
18	5	126
19	0	129

TABLE 6

No.	Mol.% hydroquinone	M.p., °
1	100	171
2	90	166
3	80	158
4	70	150
5	60	142
6	50	132
7	40	117
8	35	110
9	31	98
10	30	95
11	29	94
12	25	92
13	21	85
14	20	83
15	19	85
16	15	91
17	10	96
18	0	103

TABLE 7

No.	Mol. % urea	M.p., °
1	100	133
2	90	123
3	80	112
4	78	110
5	77	109
6	76	110
7	75	111
8	70	116
9	65	119
10	60	120
11	55	120
12	50	117
13	47	114
14	46	113
15	45	115
16	40	122
17	30	134
18	20	143
19	10	152
20	0	158

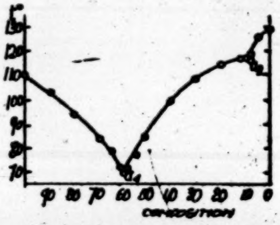

Fig. 5. Section: resorcinol - 50 mol.% urea and 50 mol.% hydroquinone.

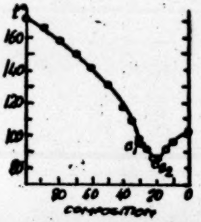

Fig. 6. Section: hydroquinone - 50 mol.% urea and 50 mol.% resorcinol.

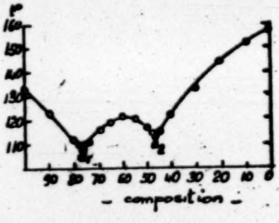

Fig. 7. Section: urea - 80 mol.% hydroquinone and 20 mol.% resorcinol.

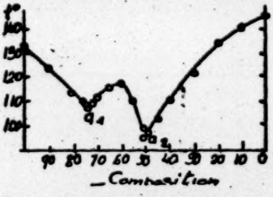

Fig. 8. Section: urea - 60 mol.% hydroquinone and 40 mol.% resorcinol.

TABLE 8

No.	Mol.% urea	M.p., °
1	100	133
2	90	124
3	80	113
4	75	109
5	74	108
6	73	107
7	72	109
8	70	111
9	65	115
10	60	117.5
11	55	110
12	51	98
13	50	95
14	49	97
15	45	103
16	40	110
17	30	120
18	20	133
19	10	141
20	0	145

TABLE 9

No.	Mol.% urea	M.P., °
1	100	133
2	90	124
3	80	114
4	70	98
5	66	91
6	65	90
7	64	92
8	60	98
9	55	101
10	50	103
11	45	100
12	40	95
13	36	90
14	35	89
15	34	88
16	33	89
17	30	93
18	20	106
19	10	115
20	0	120

TABLE 10

No.	Mol.% urea	M.p., °
1	100	133
2	90	124
3	80	111
4	70	90
5	69	88
6	68	85
7	67	86
8	65	87
9	60	92
10	50	95
11	40	93
12	30	86
13	25	81
14	22	79
15	21	78
16	20	79
17	15	84
18	10	88
19	0	97

TABLE 11

No.	Mol. % urea	M.p., °
1	100	133
2	90	122
3	80	113
4	76	110
5	75	108.5
6	74	110
7	70	114
8	65	117
9	60	119
10	55	116
11	50	110
12	49	108
13	48	109
14	45	112
15	40	117
16	30	130
17	20	140
18	10	145
19	0	150

TABLE 12

No.	Mol. % hydroquinone	M.P., °
1	100	171
2	90	165
3	80	159
4	70	151
5	60	144
6	50	135
7	40	127.5
8	30	100
9	25	86
10	23	75
11	20	70
12	19	73
13	15	78
14	10	83
15	0	85

TABLE 13

No.	Mol.% hydroquinone	M.p., °
1	100	133
2	90	124
3	80	112
4	70	94
5	68	90
6	67	88
7	66	88.5
8	65	89
9	60	90
10	55	91
11	51	89
12	50	89.5
13	45	89
14	40	88
15	30	80
16	28	77
17	27	75
18	26	76
19	25	77
20	20	83
21	10	87
22	0	88

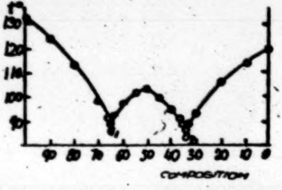

Fig. 9. Section: urea – 60 mol.% resorcinol and 40 mol.% hydroquinone.

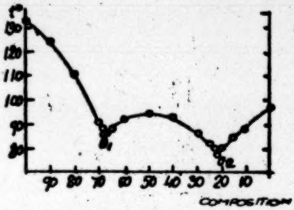

Fig. 10. Section: urea – 80 mol.% resorcinol and 20 mol.% hydroquinone.

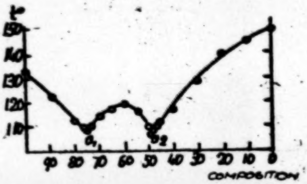

Fig. 11. Section: urea – 70 mol.% hydroquinone and 30 mol.% resorcinol.

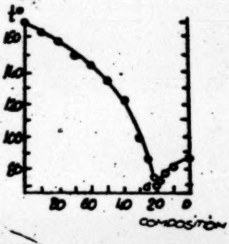

Fig. 12. Section: hydroquinone – 75 mol% resorcinol and 25 mol.% urea.

Section: urea – 60 mol.% hydroquinone and 40 mol.% resorcinol, (Table 8, Fig. 8). a_1 at 73 mol.% urea with m.p. 107°; a_2 at 50 mol.% urea, with a m.p. of 95°.

Section: urea – 60 mol.% resorcinol and 40 mol.% hydroquinone (Table 9, Fig. 9). a_1 at 65 mol.% urea, with a m.p. of 90°; a_2 at 34 mol.% urea, with a m.p. of 88°.

Section: urea – 80 mol.% resorcinol and 20 mol.% hydroquinone (Table 10, Fig. 10). a_1 at 68 mol.% urea, with a m.p. of 85°; a_2 at 21 mol.% urea, with a m.p. of 78°.

Section: urea – 70 mol.% hydroquinone and 30 mol.% resorcinol (Table 11, Fig. 11). a_1 at 75 mol.% urea with a m.p. of 108.5°; a_2 at 49 mol.% urea, with a m.p. of 108°.

Section: hydroquinone – 75 mol.% resorcinol and 25 mol.% urea (Table 12, Fig. 12). a at 20 mol.% hydroquinone, with a m.p. of 70°.

Section: urea – 70 mol.% resorcinol and 30 mol.% hydroquinone. (Table 13, Fig. 13). a_1 at 67 mol.% urea, with a m.p. of 88°; a_2 at 51 mol.% urea, with a m.p. of 89°; a_3 at 27 mol.% urea with m.p. of 75°.

Section: hydroquinone – 55 mol.% resorcinol and 45 mol.% urea, (Table 14, Fig. 14). a at 23 mol % hydroquinone, with a m.p. of 80°.

Section: hydroquinone – 60 mol.% urea and 40 mol.% resorcinol (Table 15, Fig. 15). a_1 at 33 mol.% hydroquinone with a m.p. of 97°; a_2 at 15 mol.% hydroquinone with a m.p. of 89°.

TABLE 14

No.	Mol.% hydroquinone	M.p., °
1	100	171
2	90	161
3	80	158
4	70	150
5	60	143
6	50	134
7	40	119
8	30	97
9	25	85
10	24	83
11	23	80
12	22	82
13	20	83
14	10	94
15	0	101

TABLE 15

No.	Mol.% hydroquinone	M.p., °
1	100	171
2	90	165
3	80	156
4	70	148
5	60	140
6	50	129
7	40	116
8	35	106
9	34	102
10	33	97
11	32	99
12	30	102
13	25	103
14	20	101
15	16	94
16	15	89
17	14	90
18	10	93
19	0	99

TABLE 16

No.	Mol.% hydroquinone	M.p., °
1	100	171
2	90	163
3	80	155
4	70	148
5	60	137
6	50	126
7	40	114
8	35	105
9	32	99
10	31	96
11	30	98
12	25	106
13	20	105
14	15	97
15	10	87
16	9	85.5
17	8	87
18	5	91
19	0	93

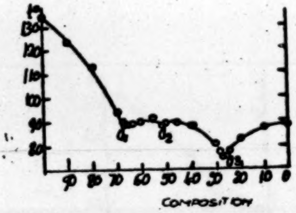

Fig. 13. Section: urea – 70 mol. % resorcinol and 30 mol.% hydroquinone.

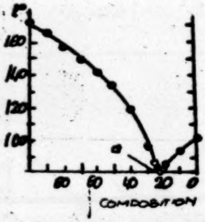

Fig. 14. Section: hydroquinone – 55 mol.% resorcinol and 45 mol.% urea.

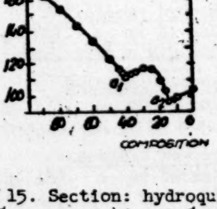

Fig. 15. Section: hydroquinone – 60 mol.% urea and 40 mol.% resorcinol.

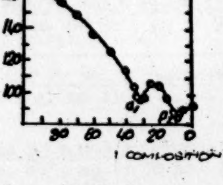

Fig. 16. Section: hydroquinone – 70 mol.% urea and 30 mol.% resorcinol.

TABLE 17

No.	Mol.% hydroquinone	M.p., °
1	100	171
2	90	162
3	80	154
4	70	144
5	60	134
6	50	123
7	45	117
8	42.5	114
9	40	112
10	37.5	113
11	35	115
12	30	117
13	25	117
14	20	110
15	17.5	104
16	15	97
17	12.5	98
18	10	95
19	0	105

TABLE 18

No.	Mol.% hydroquinone	M.p., °
1	100	110
2	90	108
3	80	98
4	70	82
5	69	80
6	68	81
7	65	83
8	60	86
9	50	88
10	40	88
11	39	87.5
12	38	87
13	37	89
14	35	95
15	30	103
16	21	108
17	20	108
18	19	110
19	10	119
20	0	120

TABLE 19

No.	Mol.% hydroquinone	M.p., °
1	100	110
2	90	104
3	80	95
4	70	85
5	66	80
6	65	79
7	64	79.5
8	60	80.5
9	50	81
10	43	80.2
11	42	80
12	41	83.5
13	40	85.3
14	30	102
15	25	100
16	23	97
17	22	96
18	20	98
19	18	99
20	17	106
21	10	120
22	0	126

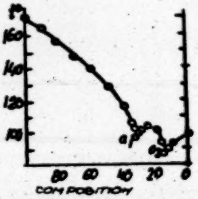

Fig. 17. Section hydroquinone - 80 mol.% urea and 20 mol.% resorcinol.

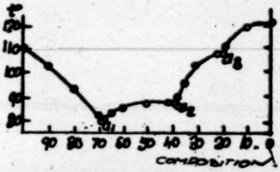

Fig. 18. Section: resorcinol - 70 mol.% urea and 30 mol.% hydroquinone.

Section: hydroquinone - 70 mol.% urea and 30 mol.% resorcinol (Table 16, Fig. 16). a_1 at 31 mol.% hydroquinone, with a m.p. of 96°; a_2 at 9 mol.% hydroquinone, with a m.p. of 85.5°.

Section: hydroquinone - 80 mol.% urea and 20 mol.% resorcinol (Table 17, Fig. 17). a_1 at 40 mol.% hydroquinone, with a m.p. of 112°; a_2 at 15 mol.% hydroquinone, with a m.p. of 97°.

Section: resorcinol - 70 mol.% urea and 30 mol.% hydroquinone (Table 18, Fig. 18). a_1 at 69 mol.% resorcinol, with m.p. 80°; a_2 at 38 mol.% resorcinol, with m.p. 87°; a_3 at 20 mol.% resorcinol, with m.p. 108°.

TABLE 20

No.	Mol.% of 50% urea and 50% hydroquinone	M.P.,°	No.	Mol.% of 50% urea and 50% hydroquinone	M.p., °	No.	Mol.% of 50% urea and 50% hydroquinone	M.p., °
1	100	129.2	8	57.5	100.5	14	30	88
2	90	126	9	55	105	15	27.5	90
3	80	117	10	50	109	16	25	92
4	70	105	11	40	105	17	20	95
5	65	100	12	35	98	18	10	100
6	62.5	97	13	32.5	93	19	0	103.5
7	60	95						

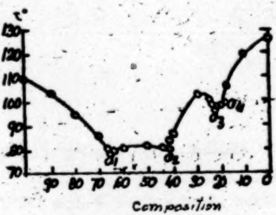

Fig. 19. Section: resorcinol – 60 mol.% urea and 40 mol.% hydroquinone.

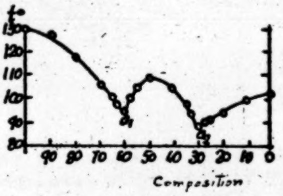

Fig. 20. Section: 50 mol.% urea and 50 mol.% hydroquinone – 50 mol.% urea and 50 mol.% resorcinol.

Section: resorcinol – 60 mol.% urea and 40 mol.% hydroquinone (Table 19, Fig. 19). a_1 at 65 mol.% resorcinol, with m.p. 79°; a_2 at 42 mol.% resorcinol, with a m.p. of 80°; a_3 at 22 mol.% resorcinol, with a m.p. of 96°; and a_4 at 18 mol.% resorcinol, with m.p. of 99°.

Section: 50 mol.% urea + 50 mol.% hydroquinone – 50 mol.% urea + 50 mol.% resorcinol, (Table 20 and Fig. 20). a_1 at 60 mol.% (50 mol.% urea + 50 mol.% hydroquinone), with a m.p. of 95°; a_2 at 30 mol.% (50 mol.% urea and 50 mol.% hydroquinone), with a m.p. of 88°.

We used the data for the three binary systems and the 17 sections to plot the crystallization surface of the urea – hydroquinone – resorcinol ternary system on a Gibbs triangular diagram (Fig. 21).

The crystallization surface exhibited a maximum for a ternary compound with a congruent melting point and the composition of 50 mol.% urea, 25 mol.% resorcinol, and 25 mol.% hydroquinone: $2CO(NH_2)_2 \cdot \underline{m}\text{-}C_6H_4(OH)_2 \cdot p\text{-}C_6H_4(OH)_2$, with m.p. 109°.

This maximum is flatter on the side of the compound $[CO(NH_2)_2 \cdot \underline{m}\text{-}C_6H_4(OH)_2]$. The shape of the maximum indicates that the ternary compound is dissociated considerably in the molten state.

The crystallization surface of the ternary system consists of six areas: The first area AaE_2E_3C – crystallization of urea; the second area $BbE_1E_4E_5e$ – crystallization of hydroquinone; the third area CdE_5e – crystallization of resorcinol; the fourth area aE_2E_1b – crystallization of the compound $CO(NH_2)_2 \cdot p\text{-}C_6H_4(OH)_2$; the fifth area $cE_3E_4E_5c$ – crystallization of the compound $CO(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2$; and the sixth area $E_1E_2E_3E_4$ – crystallization of the ternary compound

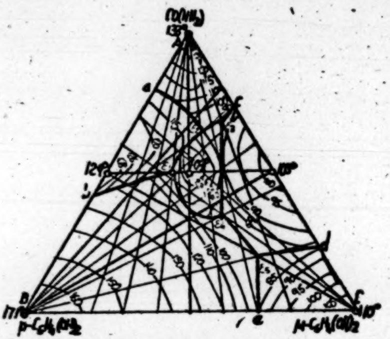

Fig. 21.

$2CO(NH_2)_2 \cdot p\text{-}C_6H_4(OH)_2 \cdot m\text{-}C_6H_4(OH)_2$.

There are five ternary invariant points in the system: E_1 at 50 mol.% urea, 20 mol.% resorcinol, and 30 mol.% hydroquinone, with a m.p. of 95°; E_2 at 65 mol.% urea, 14 mol.% hydroquinone, and 21 mol.% resorcinol, with a m.p. of 90° – a transition point; E_3 at 68 mol.% urea, 6.5 mol.% hydroquinone, and 25.5 mol.% resorcinol, with a m.p. of 85° – a eutectic point; E_4 at 23 mol.% of hydroquinone, 42 mol.% resorcinol, and 35 mol.% urea, with a m.p. of 80° – a transition point; and E_5 at 60 mol.% resorcinol, 20 mol.% hydroquinone, and 20 mol.% urea, with a m.p. of 70°, a eutectic point.

SUMMARY

1. The crystallization surface of the ternary system: urea – resorcinol – hydroquinone, has been investigated by the visual polythermal method of physicochemical analysis.

2. A ternary compound with a congruent melting point, $2CO(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2 \cdot p\text{-}C_6H_4(OH)_2$, with 50 mol.% urea, 25 mol.% resorcinol, and 25 mol.% hydroquinone and a m.p. of 109° has been found.

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RESEARCH ON THE REACTION BETWEEN IONS OF BIVALENT MANGANESE AND $K_4Fe(CN)$.

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As has been demonstrated in several investigations, including our own [1], the formation of normal ferrocyanides of the heavy metals, (which are slightly soluble, as a rule) usually does not take place when potassium ferrocyanide is used as the precipitating agent. The basic reason for this is the tendency of the potassium ferrocyanide to precipitate together with the ferrocyanide of the heavy metal as a double salt or a solid solution. The presence of the latter, especially in systems of the ferrocyanides of cobalt and nickel and of potassium, has been proved by I.V.Tananaev and M.I.Levina [2]. Examination of the experimental data on systems consisting of ferrocyanides of this type indicates that, although the basic forms of interaction repeat themselves in such systems, qualitatively speaking, the quantitative relationships between the ions of the alkali and heavy metals may vary very considerably. Nickel ions, for instance, react with potassium ferrocyanide to form solid solutions and the double salt $2Ni_2Fe(CN)_6 \cdot K_4Fe(CN)_6$, though $5CO_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ and $4CO_2Fe(CN)_6 \cdot 3K_4Fe(CN)_6$ are formed by cobalt ions under exactly the same conditions. Hence, to prepare a ferrocyanide of a certain composition we must know the exact proportions of the reagents in the original solution governing the formation of the given salt.

The present paper describes the results of a study of the reaction between ions of bivalent manganese ($MnSO_4$) and $K_4Fe(CN)_6$ in aqueous solution, at various concentrations and proportions of the reacting salts. The investigation employed the methods of physico-chemical analysis: solubilities and conductances. Two types of solubility tests were run: with a constant amount of $MnSO_4$ and varying amounts of $K_4Fe(CN)_6$, and with varying percentages of both constituents.

Tests with a Constant Percentage of $MnSO_4$ in the Original Mixture

Enough $MnSO_4$ (40 ml of a 0.1 N solution) was placed in a 250 ml measuring flask to make the original concentration of this salt 0.0156 mol per liter. Then water was added to the flask, plus the $K_4Fe(CN)_6$ solution (the amount of the solution rising from one test to the next), the total added being such as to make the total final volume of the system 250 ml. Then the flask was placed in a thermostat, and its contents (liquid plus precipitate) were motor-stirred for one hour at 25° ± 0.1°. After the contents had settled in the thermostat, a sample was taken of the transparent solution, which was analyzed for its manganese content, as determined by a Volhard titration. This enabled us to determine (by differences) the amount of reacted (precipitated) manganese. In view of the fact that no $Fe(CN)_6''''$ ions were ever found in any one of the samples (titrating in an acid medium with potassium permanganate), we were certain that all the $Fe(CN)_6''''$ ions placed in the system had gone into the precipitate. The numerical data on the manganese, with the known initial quantity of the $K_4Fe(CN)_6$, made it easy to calculate the ratio between the two in the solid phase, thus essentially determining the composition of the precipitate.*

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*The problem of the water of crystallization cannot be solved in this manner, of course, but we were not interested in that.

The data on the composition of the precipitate formed in this system are listed in Table 1. As we see by comparing the figures in Cols. 4 and 9, the $Mn^{\cdot\cdot}:Fe(CN)_6''''$ ratio in the precipitate remains practically constant, close to unity, as the ratio of the same constituents in the initial mixture is increased from 0.125 to 0.805. This is shown quite clearly in Fig. 1; the experimental line representing the interaction has practically the theoretical slope calculated on the assumption that the double salt $Mn_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ is formed. It follows that the precipitate is the foregoing double salt, no manganese ferrocyanide of normal composition thus being produced at the given concentrations of $MnSO_4$ and $K_4Fe(CN)_6$. This seems somewhat strange in view of the fact that at the ratios set forth in Table 1 a precipitate is thrown down in the presence of an excess of manganese ions. The tendency of the latter to prevent the formation of the double salt

TABLE 1

Data on the Solubilities in the $MnSO_4$ – $K_4Fe(CN)_6$ – H_2O System With a Constant Amount of $MnSO_4$ in the Initial Mixture

Test No.	0.1 m $MnSO_4$ (ml)	0.1 m. $K_4Fe(CN)_6$ (ml)	$Fe(CN)_6''''$: $Mn^{\cdot\cdot}$ in the initial mixture	Mn in the initial mixture mols/liter	Mn in the supernatant solution, mols/liter	Reacted mols per liter		$Mn^{\cdot\cdot}$: $Fe(CN)_6''''$ in the precipitate	K in the supernatant solution, mols/liter
						Mn	$Fe(CN)_6$		
1	2	3	4	5	6	7	8	9	10
1	39	5.00	0.128	0.0156	0.0137	0.0019	0.002	0.95	0.0040
2		10.00	0.256		0.0115	0.0041	0.004	1.025	0.0080
3		15.00	0.384		0.0094	0.0062	0.0061	1.02	0.0122
4		18.00	0.460		0.0081	0.0075	0.0072	1.02	0.0144
5		19.40	0.500		0.0074	0.0082	0.0078	1.04	0.0156
6		20.00	0.510		0.0072	0.0084	0.008	1.05	0.0160
7		22.00	0.564		0.0064	0.0092	0.0088	1.045	0.0176
8		28.00	0.718		0.0038	0.00118	0.0112	1.05	0.0224
9		30.00	0.770		0.00315	0.01245	0.0120	1.03	0.0240
10		32.20			Precipitate peptized				

$$Mn^{2+} + K_2MnFe(CN)_6 \longrightarrow Mn_2Fe(CN)_6 + 2K^+$$

is apparently opposed by the more pronounced reverse tendency of the potassium ions, which accumulate in the solution as the precipitate is thrown down:

$$Mn^{2+} + K_4Fe(CN)_6 \longrightarrow K_2MnFe(CN)_6 + 2K^+.$$

But, as we see in Test No. 1, in which the percentages of manganese and of potassium were a maximum and a minimum, respectively, the composition of the precipitate did not differ appreciably from that of the double salt, even though the absolute concentration of the potassium ions in the equilibrium solution was fairly low (0.004 mol/liter). It follows that the tendency of the manganese to form a binary ferrocyanide with the potassium ions is quite pronounced, being due, probably, to the fact that the solubility of the double salt is much lower than that of the normal salt.*

As we see from Test No. 10 (Table 1), when the $Mn^{\cdot\cdot}:Fe(CN)_6''''$ ratio in the original mixture was 0.8, the precipitate was peptized, forming a stable sol that did not coagulate for a long time. We were, therefore, unable to make a study of the system at high $K_4Fe(CN)_6$ concentrations. But, as will be seen subsequently, a precipitate is thrown down again when there is an appreciable excess of $K_4Fe(CN)_6$ in the equilibrium solution, the composition of the precipitate remaining unchanged. No such ratios between the $MnSO_4$ and the $K_4Fe(CN)_6$ were realized in this series of tests, however.

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*A similar phenomenon is observed, for instance, in the formation of alums, which are less soluble than $Al_2(SO_4)_3$ or K_2SO_4.

Tests with Varying Concentrations of $MnSO_4$ and $K_4Fe(CN)_6$

(Triangle Diagram Method)

In this procedure, the variable $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratios were achieved by simultaneously changing the concentrations of the $MnSO_4$ and the $K_4Fe(CN)_6$. The tests were run in series at the following constant concentrations:

$\Sigma MnSO_4 + K_4Fe(CN)_6$: $6\cdot10^{-4}$, $8\cdot10^{-4}$, $1\cdot10^{-3}$, $2\cdot10^{-3}$, $4\cdot10^{-3}$, $6\cdot10^{-3}$, $8\cdot10^{-3}$, $1\cdot10^{-2}$, $3\cdot10^{-2}$, and $1\cdot10^{-1}$ mol/liter.

The following ratios were used in all the series:

$Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$: 10.5, 2.5, 2, 1.67, 1.25, 1.18, 1.11, 1.05, 10.5, 0.25, and 0.1. The location of the sections passed through the triangular diagram on a logarithmic scale is shown in Fig. 2.* In this way we plotted 130 points in the triangular diagram experimentally, the base of which was $\Sigma MnSO_4 + K_4Fe(CN)_6 =$ = 0.1 mol/liter.

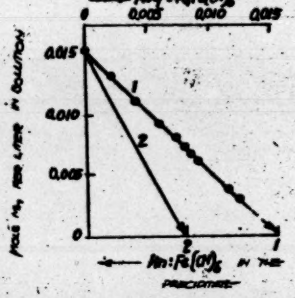

Fig. 1. $MnSO_4 - K_4Fe(CN)_6 - H_2O$ system. $MnSO_4$ - 0.0156 mol/liter.

1) $Mn_2Fe(CN)_6 \cdot K_4Fe(CN)_6$; 2) $Mn_2Fe(CN)_6$.

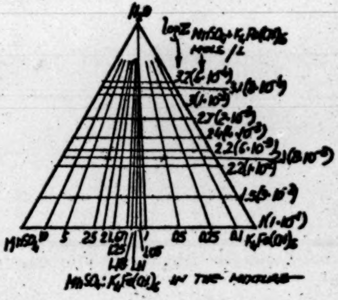

Fig. 2. $MnSO_4 - K_4Fe(CN)_6 - H_2O$ System. Location of sections.

The solutions were mixed in the same manner as described above for the tests using a constant concentration of $MnSO_4$. The total volume of the system was 250 ml. The mixing time was 1 hour; the temperature was 25°. When the manganese content of the equilibrium solution was extremely small (below $1\cdot10^{-3}$ mol/liter), the manganese was determined colorimetrically by the silver-persulfate method.

Part of each sample taken from the transparent equilibrium solutions was used to measure the conductance.

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*Figure 2 is shown simply as an illustration of the method of making the sections and serves no other purpose.

TABLE 2

Solubility and Conductance in the $MnSO_4 - K_4Fe(CN)_6 - H_2O$ System at 25°

Test No.	Mn: Fe(CN)$_6$ in the initial mixture	Section I $\Sigma MnSO_4 + K_4Fe(CN)_6 = 6\cdot10^{-4}$ mol/l.			Section II $\Sigma MnSO_4 + K_4Fe(CN)_6 = 8\cdot10^{-4}$ mol/l.			Section III $\Sigma MnSO_4 + K_4Fe(CN)_6 =$
		Mn after precipitation, mols/liter	Mn: Fe(CN)$_6$ in precipitate	Specific conductance	Mn after precipitation, mols/liter	Mn: Fe(CN)$_6$ in precipitate	Specific conductance	Mn after precipitation, mols/liter
1	10	$4.5\cdot10^{-4}$	1.76	$1.37\cdot10^{-4}$	$6.13\cdot10^{-4}$	1.57	$1.88\cdot10^{-4}$	$7.49\cdot10^{-4}$
2	5	$3.07\cdot10^{-4}$	1.94	$1.39\cdot10^{-4}$	$4.48\cdot10^{-4}$	1.63	$1.96\cdot10^{-4}$	$5.35\cdot10^{-4}$
3	2.5	$1.34\cdot10^{-4}$	1.70	$1.33\cdot10^{-4}$	$1.71\cdot10^{-4}$	1.74	$1.79\cdot10^{-4}$	$2.31\cdot10^{-4}$
4	2	$1.3\cdot10^{-4}$	1.35	$1.28\cdot10^{-4}$	$2.01\cdot10^{-4}$	1.17	$1.7\cdot10^{-4}$	$2.53\cdot10^{-4}$
5	1.67	$1.07\cdot10^{-4}$	1.29	$1.18\cdot10^{-4}$	$1.7\cdot10^{-4}$	1.1	$1.62\cdot10^{-4}$	$2.22\cdot10^{-4}$
6	1.25	$4.23\cdot10^{-5}$	1.09	$1.08\cdot10^{-4}$	$4.87\cdot10^{-5}$	1.1	$1.56\cdot10^{-4}$	$8.4\cdot10^{-5}$
7	1.18	$9.65\cdot10^{-6}$	1.1	$1.68\cdot10^{-4}$	$4.35\cdot10^{-5}$	1.05	$1.83\cdot10^{-4}$	$5.79\cdot10^{-5}$
8	1.11	$9.65\cdot10^{-6}$	1.07	$1.87\cdot10^{-4}$	$4.83\cdot10^{-5}$	0.98	$1.66\cdot10^{-4}$	Traces
9	1.05	$9.65\cdot10^{-6}$	1.02	$1.96\cdot10^{-4}$	Traces	1.05	$2.06\cdot10^{-4}$	-
10	1	Sol		$1.2\cdot10^{-4}$	Sol		$1.69\cdot10^{-4}$	Sol
11	0.5			$2\cdot10^{-4}$			$3\cdot10^{-4}$	
12	0.25			$2.78\cdot10^{-4}$			$3.96\cdot10^{-4}$	
13	0.1			$3.3\cdot10^{-4}$			$4.6\cdot10^{-4}$	

		Section VI $\Sigma MnSO_4 + K_4Fe(CN)_6 = 6\cdot10^{-3}$ mols/l.			Section VII $\Sigma MnSO_4 + K_4Fe(CN)_6 = 8\cdot10^{-3}$ mols/l.			Section $\Sigma MnSO_4 + K_4Fe(CN)_6 =$
1	10	$4.28\cdot10^{-3}$	2.1	$1.07\cdot10^{-3}$	$5.75\cdot10^{-3}$	2.08	$1.36\cdot10^{-3}$	$7.35\cdot10^{-3}$
2	5	$3.78\cdot10^{-3}$	1.22	$1.03\cdot10^{-3}$	$5.08\cdot10^{-3}$	1.18	$1.32\cdot10^{-3}$	$6.43\cdot10^{-3}$
3	2.5	$2.41\cdot10^{-3}$	1.09	$1.1\cdot10^{-3}$	$3.29\cdot10^{-3}$	1.06	$1.24\cdot10^{-3}$	$4.06\cdot10^{-3}$
4	2	$1.85\cdot10^{-3}$	1.075	$9.7\cdot10^{-4}$	$2.6\cdot10^{-3}$	1.03	-	$3.06\cdot10^{-3}$
5	1.67	$1.34\cdot10^{-3}$	1.07	$9.5\cdot10^{-4}$	$1.83\cdot10^{-3}$	1.03	$1.27\cdot10^{-3}$	$2.25\cdot10^{-3}$
6	1.25	$5.44\cdot10^{-4}$	1.05	$9.2\cdot10^{-4}$	$7.45\cdot10^{-4}$	1.04	$1.19\cdot10^{-3}$	$8.41\cdot10^{-4}$
7	1.18	-	-	-	$3.76\cdot10^{-4}$	1.07	$1.22\cdot10^{-3}$	$5.3\cdot10^{-4}$
8	1.11	$1.35\cdot10^{-4}$	1.06	$9.37\cdot10^{-4}$	$1.5\cdot10^{-4}$	1.07	$1.21\cdot10^{-3}$	$2.9\cdot10^{-4}$
9	1.05	$4.83\cdot10^{-5}$	1.05	$9.26\cdot10^{-4}$	$1.93\cdot10^{-5}$	1.06	$1.18\cdot10^{-3}$	$9.65\cdot10^{-8}$
10	1	Sol		$1.14\cdot10^{-3}$	Sol		$1.31\cdot10^{-3}$	Sol
11	0.5			$1.8\cdot10^{-3}$			$2.27\cdot10^{-3}$	
12	0.25			$2.3\cdot10^{-3}$			$3.04\cdot10^{-3}$	
13	0.1			$2.6\cdot10^{-3}$			$3.4\cdot10^{-3}$	

TABLE 2

Solubility and Conductance in the $MnSO_4 - K_4Fe(CN)_6 - H_2O$ System at 25°

Section III $1\cdot10^{-3}$ mols/liter		Section IV $\Sigma MnSO_4 + K_4Fe(CN)_6 = 2\cdot10^{-3}$ mols/liter			Section V $\Sigma MnSO_4 + K_4Fe(CN)_6 = 4\cdot10^{-3}$ mols/liter		
Mn: $Fe(CN)_6$ in the initial mixture	Specific conductance	Mn after precipitation, Mols/liter	Mn: $Fe(CN)_6$ in the initial mixture	Specific conductance	Mn after precipitation, mols/liter	Mn: $Fe(CN)_6$ in the initial mixture	Specific conductance
1.72	$2.54\cdot10^{-4}$	$1.47\cdot10^{-3}$	1.92	$4.12\cdot10^{-4}$	$2.83\cdot10^{-3}$	2.22	$7.3\cdot10^{-4}$
1.84	$2.36\cdot10^{-4}$	$1.03\cdot10^{-3}$	1.93	$4.18\cdot10^{-4}$	$2.31\cdot10^{-3}$	1.53	$7.5\cdot10^{-4}$
1.71	$2.34\cdot10^{-4}$	$7.74\cdot10^{-4}$	1.14	$3.7\cdot10^{-4}$	$1.6\cdot10^{-3}$	1.05	$7.37\cdot10^{-4}$
1.24	$2.24\cdot10^{-4}$	$6.2\cdot10^{-4}$	1.065	$3.56\cdot10^{-4}$	$1.22\cdot10^{-3}$	1.08	$7.4\cdot10^{-4}$
1.08	$2.1\cdot10^{-4}$	$4.39\cdot10^{-4}$	1.08	$3.38\cdot10^{-4}$	$8.98\cdot10^{-4}$	1.07	$7.04\cdot10^{-4}$
1.07	$2.25\cdot10^{-4}$	$1.81\cdot10^{-4}$	1.04	–	–	–	$7.04\cdot10^{-4}$
1.05	$1.96\cdot10^{-4}$	$9.68\cdot10^{-5}$	1.06	$3.5\cdot10^{-4}$	$1.55\cdot10^{-4}$	1.09	$6.65\cdot10^{-4}$
1.1	$2.39\cdot10^{-4}$	$5.79\cdot10^{-5}$	1.08	–	$6.76\cdot10^{-5}$	1.07	$6.43\cdot10^{-4}$
–	$2.31\cdot10^{-4}$	$9.65\cdot10^{-5}$	1.04	–	$9.65\cdot10^{-6}$	1.03	$6.76\cdot10^{-4}$
	$1.9\cdot10^{-4}$	Sol		$3.4\cdot10^{-4}$	Sol		$6.6\cdot10^{-4}$
	$3.36\cdot10^{-4}$			$6.3\cdot10^{-4}$			$1.22\cdot10^{-4}$
	$3.89\cdot10^{-4}$			$8.4\cdot10^{-4}$			$1.6\cdot10^{-3}$
	$5.08\cdot10^{-4}$			$1\cdot10^{-3}$			$1.8\cdot10^{-3}$

VIII $1\cdot10^{-2}$ mols/liter		Section IX $\Sigma MnSO_4 + K_4Fe(CN)_6 = 3\cdot10^{-2}$ mols/liter			Section X $\Sigma MnSO_4 + K_4Fe(CN)_6 = 1\cdot10^{-1}$ mols/liter		
1.9	$1.6\cdot10^{-3}$	$2.45\cdot10^{-2}$	1.08	$3.97\cdot10^{-3}$	$8.15\cdot10^{-2}$	1.03	$1.02\cdot10^{-2}$
1.13	$1.6\cdot10^{-3}$	$2\cdot10^{-2}$	1.02	$4.13\cdot10^{-3}$	–	–	–
1.07	$1.56\cdot10^{-3}$	$1.24\cdot10^{-2}$	1.05	$4.12\cdot10^{-3}$	$4.21\cdot10^{-2}$	1.02	$1.08\cdot10^{-2}$
1.08	$1.53\cdot10^{-3}$	–	–	–	$3.27\cdot10^{-2}$	1.02	$1.12\cdot10^{-2}$
1.06	$1.5\cdot10^{-3}$	$7.24\cdot10^{-2}$	1.02	$3.98\cdot10^{-3}$	$2.38\cdot10^{-2}$	1.03	$1.13\cdot10^{-2}$
1.06	$1.5\cdot10^{-3}$	$2.75\cdot10^{-3}$	1.04	$3.97\cdot10^{-3}$	$9.29\cdot10^{-3}$	1.04	$1.15\cdot10^{-2}$
1.06	$1.46\cdot10^{-3}$	$2.1\cdot10^{-3}$	1.02	$4.02\cdot10^{-3}$	$6.16\cdot10^{-3}$	1.04	$1.15\cdot10^{-2}$
1.04	–	$1.06\cdot10^{-3}$	1.02	$3.96\cdot10^{-3}$	$3.62\cdot10^{-3}$	1.03	$1.15\cdot10^{-2}$
1.05	–	Sol		$4.08\cdot10^{-3}$	Sol		$1.2\cdot10^{-2}$
	$1.54\cdot10^{-3}$	1·10Sol		$4.32\cdot10^{-3}$	None	1.08	$1.28\cdot10^{-2}$
	$2.6\cdot10^{-3}$		1.02	$7.09\cdot10^{-3}$	None	1.05	$2.01\cdot10^{-2}$
	$3.4\cdot10^{-3}$	–	1.00	$9.11\cdot10^{-3}$	None	1.06	$2.59\cdot10^{-2}$
	–	$1.9\cdot10^{-5}$	0.98	$1.07\cdot10^{-2}$	None	1.05	$3.07\cdot10^{-2}$

Our measurements are tabulated in Table 2, which gives the following quantities for each section representing a certain value of $\Sigma MnSO_4 + K_4Fe(CN)_6$: the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the initial mixture; the manganese ion concentration in the equilibrium solution; the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the precipitate; and the conductance of the equilibrium solution. We see from Table 2 that the manganese concentration in the equilibrium solution drops regularly for each mixture as the amount of $K_4Fe(CN)_6$ added increases. This is illustrated in Fig. 3 by the curves showing the logarithm of the manganese concentration as a function of the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the initial mixture. It is readily seen that the shape of the curves varies with the $\Sigma MnSO_4 + K_4Fe(CN)_6$ concentration in the original mixture. The curves are somewhat irregular in the first four sections ($6 \cdot 10^{-4}$ - $2 \cdot 10^{-3}$ mol/liter of the aggregate salts), which may be attributed to the excessively low concentration of the reagents, but the later curves display a certain smoothness, the usual evidence of a monotonous process. All the curves, however, exhibit a decrease in the concentration of manganese in the solution down to analytically undetectable values, after which the precipitate is suddenly peptized, and analysis of the solution has to be broken off. It is typical that in all the sections investigated the formation of a sol sets in when the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio is very close to unity. This result indicates that manganese ions can be titrated with $K_4Fe(CN)_6$, using the formation of a sol as the titration end point. This has been done by D.I.Eristavi [3].

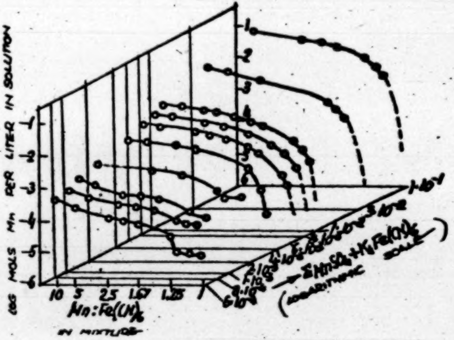

Fig. 3.

Figure 3 merely illustrates the change in the concentration of Mn^{2+} ions in the solution, without giving any idea of the composition of the precipitate thrown down at various $MnSO_4:K_4Fe(CN)_6$ ratios in the initial mixture. Figures 4-13 show the changes in the composition of the solid phase precipitated during the reaction as a function of the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the initial mixture and of the $\Sigma MnSO_4 + K_4Fe(CN)_6$. At low values of $\Sigma MnSO_4 + K_4Fe(CN)_6$, especially when the amounts of $K_4Fe(CN)_6$ placed in the system are small, the composition of the precipitate approaches that of $Mn_2Fe(CN)_6$. But even then, as the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the initial solution diminishes, the double salt begins to precipitate, thus diminishing the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the precipitate. After a certain value of the $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratio in the initial mixture, the composition of the precipitate is that of the double salt $Mn_2Fe(CN)_6 \cdot K_4Fe(CN)_6$. The location of this point shifts to the left along the axis of abscissas (toward higher $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratios) as the concentration of the aggregate reacting salts in the initial mixture increases. At $\Sigma MnSO_4 + K_4Fe(CN)_6 = 6 \cdot 10^{-4}$ mol/liter, for example, this point is located at $Mn^{\cdot\cdot}:Fe(CN)_6^{''''} \sim 1.25$. It is shifted to 1.67 in Sections II and III, to 2.5 in Section IV, etc. Even in Section VIII, with $\Sigma MnSO_4 + K_4Fe(CN)_6 = 1 \cdot 10^{-2}$ mol/liter and with very little $K_4Fe(CN)_6$ in the mixture ($Mn^{\cdot\cdot}:Fe(CN)_6''''$ = 10), the composition of the precipitate thrown down is close to that of $Mn_2Fe(CN)_6$. In Sections IX and X, however ($\Sigma MnSO_4 + K_4Fe(CN)_6$ = = $3\cdot10^{-2}$ and $1\cdot10^{-2}$ mol/liter, respectively), only the double salt is precipitated, no matter what the proportions of $MnSO_4$ and $K_4Fe(CN)_6$ in the initial mixture. Thus, the sum total of our findings is a clear picture of the interaction in the $MnSO_4 - K_4Fe(CN)_6 - H_2O$ system as it is reflected in physico-chemical analysis.

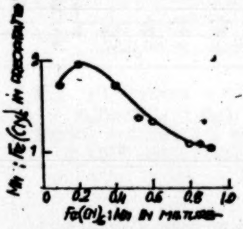

Fig. 4. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $6\cdot10^{-4}$ mol/liter

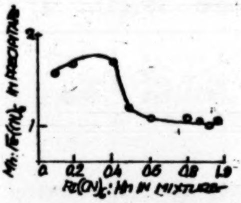

Fig. 5. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $8\cdot10^{-4}$ mol/liter.

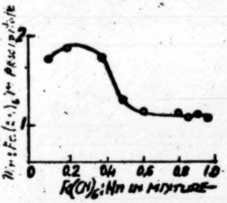

Fig. 6. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $1\cdot10^{-3}$ mol/liter.

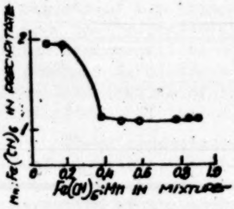

Fig. 7. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $2\cdot10^{-3}$ mol/liter.

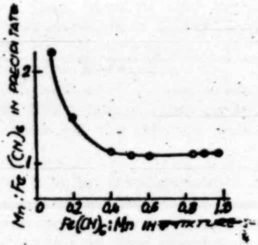

Fig. 8. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $4\cdot10^{-3}$ mol/liter.

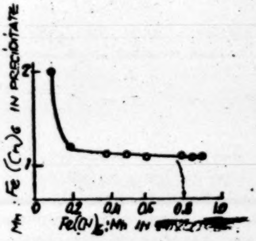

Fig. 9. System $MnSO_4$ - $K_4Fe(CN)_6 - H_2O$. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $6\cdot10^{-3}$ mol/liter.

It follows from Table 2 and Figs. 4-13 that the preparation of $Mn_2Fe(CN)_6$ and of the double salt requires the observance of special conditions. One of the principal factors affecting the change in the composition of the precipitate is, apparently, the presence of potassium ions in the solution, their concentration depending upon the quantity of $K_4Fe(CN)_6$ added. At high concentrations of $MnSO_4$ and $K_4Fe(CN)_6$ the concentration of potassium ions in the solution is so high as to precipitate the double salt all along the precipitation curve. When the double salt has to be secured at low concentrations of the reagents $MnSO_4$ and $K_4Fe(CN)_6$, an excess of potassium ions should be added to the solution, say, as KCl. As for the simple manganese ferrocyanide, it is not advisable to prepare this salt from $K_4Fe(CN)_6$; the precipitate will be contaminated with the

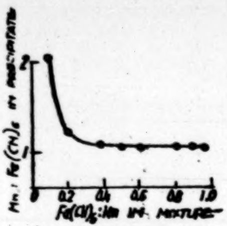

Fig. 10. System $MnSO_4$ - $K_4Fe(CN)_6$ - H_2O. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $8\cdot10^{-3}$ mol/liter.

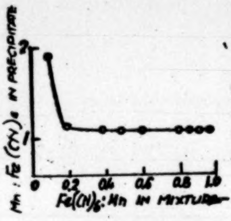

Fig. 11. System $MnSO_4$ - $K_4Fe(CN)_6$ - H_2O. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $1\cdot10^{-2}$ mol/liter.

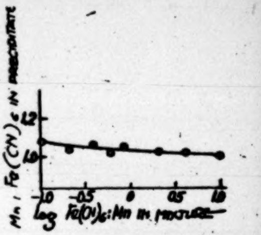

Fig. 12. System $MnSO_4$ - $K_4Fe(CN)_6$ - H_2O. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $3\cdot10^{-2}$ mol/liter.

double salt even when the optimum conditions for the formation of the single salt are employed (a large excess of $MnSO_4$ in the solution. This difficulty may be overcome by using $Li_4Fe(CN)_6$ and $H_4Fe(CN)_6$ instead of $K_4Fe(CN)_6$.

Figs. 14 and 15 illustrate the conductance of various solutions in the $MnSO_4$ - $K_4Fe(CN)_6$ - H_2O system. It is readily seen that each of the curves consists of two branches that meet at a point very close to the composition of the double salt. At high concentrations of $MnSO_4$ and $K_4Fe(CN)_6$ ($\Sigma MnSO_4 + K_4Fe(CN)_6 = 3\cdot10^{-2}$ and $1\cdot10^{-1}$ mol/liter) the intersection of the two branches of the curve coincides with the composition of the double salt.

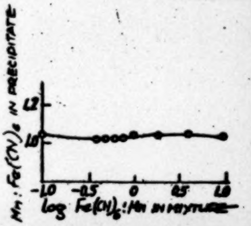

Fig. 13. System $MnSO_4$ - $K_4Fe(CN)_6$ - H_2O. $\Sigma MnSO_4 + K_4Fe(CN)_6$ = $1\cdot10^{-1}$ mol/liter.

These conductance findings indicate that it is quite feasible to perform conductometric titration of bivalent manganese ions in a solution even at extremely low concentrations of these ions. It may be that the precision of observation of the equivalence point can be improved (when titrating small percentages of manganese) by titrating in the presence of alcohol, which reduces the solubility of the precipitate.

In this connection, it is not without interest to remark that, according to Kolthoff [4], normal $Mn_2Fe(CN)_6$ is formed at first in the conductometric titration of manganese ions with $K_4Fe(CN)_6$, whereas "a salt of variable composition" is formed when the $K_4Fe(CN)_6$ is present in excess. Our data (which indicate that careful physico-chemical analysis is required to provide a correct notion of any given reaction) do not bear out the observation of Kolthoff's, which was apparently a casually made one.

In conclusion, we still have to deal with the problem of the nature of the precipitates of variable composition that are secured at certain $Mn^{\cdot\cdot}:Fe(CN)_6^{''''}$ ratios in the initial solution, and with the consequences of an analytical nature that follow from our research results on the system as a whole.

Insofar as the curves indicate (Figs. 1 et al), $Mn_2Fe(CN)_6$ does not form solid solutions with $K_4Fe(CN)_6$ (as I.V.Tananaev and M.I.Levina had found in analogous systems of nickel and cobalt [2], the variable composition of the solid phases in certain areas of the present system being due to the simultaneous precipitation of the single and double salts. The absence of solid solutions in the $MnSO_4$ – $K_4Fe(CN)_6$ – H_2O system is most convincingly shown in Fig. 1, where the slope of the line representing the interaction of $MnSO_4$ and $K_4Fe(CN)_6$ is the same as that for the double salt. It should be noted that in this respect, the system containing manganese ions is a rare example of a reaction in which a double salt is readily formed even when the solution contains an excess of ions of the heavy metal.

As for the analytical prospects opened up by these results, the following are tangible:

1. Gravimetric determination of manganese as its double salt $Mn_2Fe(CN)_6 \cdot K_4Fe(CN)_6$, inasmuch as the latter is secured very easily when $K_4Fe(CN)_6$ is used as the precipitating agent. As we have shown, the usual obstacles to the precipitation of insoluble ferrocyanides by an excess of the precipitant represented by the formation of stable colloids do not exist in the precipitation of manganese.

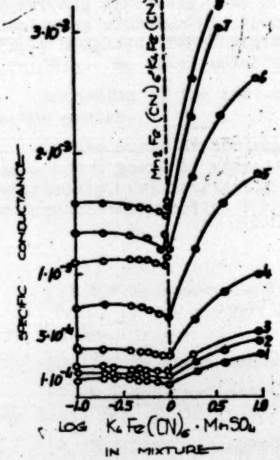

Fig. 14. Conductance of the $MnSO_4$ – $K_4Fe(CN)_6$ – H_2O System. $\Sigma MnSO_4 + K_4Fe(CN)_6$ (mol/liter): 1) $6 \cdot 10^{-4}$; 2) $8 \cdot 10^{-4}$; 3) $1 \cdot 10^{-3}$; 4) $2 \cdot 10^{-3}$; 5) $4 \cdot 10^{-3}$; 6) $6 \cdot 10^{-3}$; 7) $8 \cdot 10^{-3}$; 8) $1 \cdot 10^{-2}$.

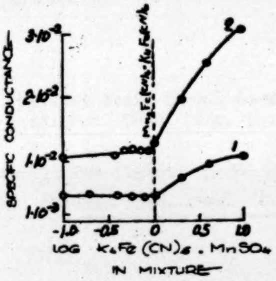

Fig. 15. Conductance of the $MnSO_4$ – $K_4Fe(CN)_6$ – H_2O system. $\Sigma MnSO_4 + K_4Fe(CN)_6$ (mol/liter): 1) $3 \cdot 10^{-2}$; 2) $1 \cdot 10^{-1}$.

2. Volumetric determination of manganese, based upon the precipitation of the double salt, the amount of which may be determined by titration with potassium permanganate in an acid medium.

3. Volumetric determination of manganese, utilizing the ability of manganese ions to form a stable sol with $K_4Fe(CN)_6$ at the equivalence point (representing the formation of the double salt).

4. Potentiometric titration of the manganese ions with $K_4Fe(CN)_6$ in the presence of an excess of potassium ions.

5. Turbidimetric determination, based upon the formation of the double salt.

6. Conductometric titration with $K_4Fe(CN)_6$, again employing the formation of the double salt.

We are now engaged in checking these conclusions in practice.

SUMMARY

The $MnSO_4$ – $K_4Fe(CN)_6$ – H_2O system has been investigated by the solubility and conductance methods of physico-chemical analysis.

It has been shown that the principal reaction product is the double salt, $Mn_2Fe(CN)_6 \cdot K_4Fe(CN)_6$, the preparation of which in the pure state requires the compliance with certain specific conditions. It has also been shown that the simple manganese ferrocyanide $Mn_2Fe(CN)_6$ cannot be prepared by the use of $K_4Fe(CN)_6$. No solid solutions were found in the system.

According to the conductance data, nothing but the double salt is formed in the system.

On the basis of the physico-chemical data secured, it is concluded that there are 6 possible ways of determining manganese by means of $K_4Fe(CN)_6$: gravimetrically, volumetrically in two ways, potentiometrically, turbidometrically, and conductometrically.

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THE DETACHMENT OF RADICALS FROM COMPLETE ASYMMETRIC DERIVATIVES OF TIN

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We have shown previously [1] that the action of light upon a chloroform solution of tetraphenyltin causes the latter to break down into diphenyldichlorotin, benzene, and hexachloroethane:

$$(C_6H_5)_4Sn + 4CHCl_3 \xrightarrow{h\nu} (C_6H_5)_2SnCl_2 + 2C_6H_6 + Cl_3CCCl_3 + 2(CHCl_2).$$

In the present paper we have endeavored to extend this reaction to the asymmetric derivatives of tin and to establish some rules governing the order in which various radicals are split off.

Frankland [2] was the first to study the reaction of hydrogen chloride and dimethyldiethyltin, but secured no clear results.

Kipping [3] reacted hydrogen chloride with triphenylbenzyltin and observed the splitting off of a phenyl group and the formation of phenylbenzyltin dichloride.

Bullard and Holden [4] made a study of the action of hydrogen chloride upon

$(CH_3)_2Sn(C_2H_5)_2$; $(C_2H_5)_2Sn(C_3H_7)_2$; and $(C_2H_5)_2Sn(C_6H_5)_2$.

In the first two cases one group of each type was split off, while in the third only phenyl was split off.

Kocheshkov and Babashinskaya [5] investigated the action of hydrogen chloride on aromatic compounds of the Ar_2SnAr_2' type. They established the following series of radicals: α-thienyl, p-anisyl, α-naphthyl, phenyl, and cyclohexyl (the electronegativity of the radicals increasing as we move toward the left). This series is a development of Kharasch's electronegativity series [6], derived from mercury compounds.

Manulkin [7] investigated the action of hydrogen chloride on compounds such as tetramethyltin and trimethylethyltin. Only one methyl group was split off. An excess of hydrogen chloride did not cause the splitting off of a second group.

Nesmeyanov and Kocheshkov [8] investigated the action of corrosive sublimate in alcohol upon Sn organic compounds of the Ar_4Sn type. The mercury can accept all four aryl groups.

Krause and Schmitz [9] reacted corrosive sublimate with ethyltriphenyltin, but they do not describe their experiments.

All that we have for the aliphatic series is an abstract of a patent by Kharasch [10]. Manulkin [7] made a study of the action of corrosive sublimate upon aliphatic compounds of the R_4Sn and R'_3SnR'' types. The conditions under which the methyl, ethyl, and heptyl groups were detached were similar. As the radical became more complex it became harder to split it off. Like hydrogen chloride and iodine, corrosive sublimate splits off the lightest radical. The splitting action of corrosive sublimate is more vigorous, however.

Manulkin investigated the detaching of radicals from organic compounds with elements of the IVth group, of the R_4M type, by reacting them with aluminum chloride and ferric chloride [18].

Frankland [2] investigated the iodination of $(CH_3)_2Sn(C_2H_5)_2$ and found that two methyl groups were split off.

Ladenburg [11] iodinated triethylphenyltin, the phenyl group splitting off.

Pope and Peachey [12] iodinated trimethylethyltin and dimethylethylpropyltin and found that the methyl group is the first one to be split off.

Naumov and Manulkin [13] investigated the iodination of organotin compounds of the R_4Sn and $R_3'SnR'$ types, where R is an alkyl radical, finding that the reaction involves the splitting off of the lightest radical.

Smith and Kipping [14] iodinated ethyltribenzyltin and found that the benzyl group – the heavier radical – was split off.

Kipping [3] made a study of the action of iodine on mixed aryl compounds of tin. He established the following sequence in which the radicals were split off: o-tolyl, p-tolyl, phenyl, and benzyl (in the order of decreasing ease of detachment).

We were interested in extending the splitting off of radicals from organotin compounds by making use of other methods: the action of U.V. light, and reactions with succinimide and bromosuccinimide. All of these methods had been previously employed with success in an investigation of the organic compounds of mercury.

This also made it possible to compare the behavior of the radicals when split off from tin and from mercury and to learn whether the order of strength of the metal – radical bond varies with the nature of the metal.

We chose diethyldiphenyltin and dibenzyldiphenyltin. The latter compound is not found in the literature. We synthesized it with a good yield from $C_6H_5CH_2MgCl$ and $(C_6H_5)_2SnCl_2$.

Dibenzyldiphenyltin was an oily substance that could not be distilled without decomposing. Thermal decomposition yielded tetraphenyltin, dibenzyl, and tin. Hence, heating involved a preliminary disproportionation reaction, tetraphenyltin and tetrabenzyltin being formed.

The photoreaction of diethyldiphenyltin and dibenzyldiphenyltin, carried out in various solvents, indicated that the phenyl groups are split off in every case, their subsequent reactions following the pattern established for the phenyl group in diphenylmercury [17]. The radical detaches hydrogen in an alcohol or chloroform solution:

$$2C_6H_5 + CH_3OH \longrightarrow 2C_6H_6 + CH_2O$$

$$C_6H_5 + CHCl_3 \longrightarrow C_6H_6 + CCl_3$$

and a chlorine atom from carbon tetrachloride:

$$C_6H_5 + CCl_4 \longrightarrow C_6H_5Cl + CCl_3.$$

The secondary CCl_3 radical then dimerizes to hexachloroethane, which has been detected in the experiments run with chloroform and carbon tetrachloride.

Thus, the first stage of the process may be represented as follows:

$$(C_2H_5)_2Sn(C_6H_5)_2 + h\nu \longrightarrow (C_2H_5)_2Sn + 2C_6H_5.$$

or

$$(C_6H_5CH_2)_2Sn(C_6H_5) + h\nu \rightarrow (C_6H_5CH_2)_2Sn + 2C_6H_5,$$

the resulting diethyltin or dibenzyltin reacting, in turn, with the solvent. In carbon tetrachloride or chloroform, this yields dichloroderivatives, which are recovered in the pure state from the reaction products:

$$(C_2H_5)_2Sn + 2CCl_4 \longrightarrow (C_2H_5)_2SnCl_2 + C_2Cl_6$$

or

$$(C_6H_5CH_2)_2Sn + 2CCl_4 \longrightarrow (C_6H_5CH_2)_2SnCl_2 + C_2Cl_6.$$

In the alcohol solution, it is likely that an alkoxy derivative, $(C_2H_5)_2Sn(OCH_3)_2$, is formed, which yields a dichloroderivative when dissolved in hydrochloric acid, thus recovering the derivative from the reaction products.

The main reaction is accompanied by various side reactions. In our experiments with diethyldiphenyltin in chloroform and carbon tetrachloride, we secured triphenyltin chloride, which may be produced as the result of a symmetrization reaction:

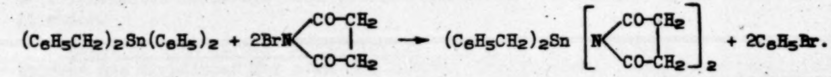
$$2(C_2H_5)_2Sn(C_6H_5)_2 \xrightarrow{h\nu} (C_2H_5)_4Sn + (C_6H_5)_4Sn$$

$$(C_6H_5)_4Sn + CHCl_3 \xrightarrow{h\nu} {}^{\cdot}C_6H_5 + (C_6H_5)_3SnCl + (CHCl_2).$$

When dibenzyldiphenyltin was irradiated for a very long time in methanol solution it decomposed still further, yielding dibenzyl and compounds of divalent tin. Evidently, the dibenzyl derivative of tin dissociated as follows:

$$(C_6H_5CH_2)_2Sn(OCH_3)_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + Sn(OCH_3)_2.$$

Other tests involving the splitting off of radicals were made on the dibenzyldiphenyltin: the action of hydrogen chloride, succinimide, and bromosuccinimide. In alcoholic solution, hydrogen chloride likewise detaches the phenyl radical, forming benzene and dibenzyltin dichloride. Fusion with succinimide causes either radical to split off – we secured a mixture of benzene and toluene. The reaction with bromosuccinimide was as follows:



$$(C_6H_5CH_2)_2Sn(C_6H_5)_2 + 2BrN\left\langle\begin{matrix}CO-CH_2\\ |\\ CO-CH_2\end{matrix}\right. \longrightarrow (C_6H_5CH_2)_2Sn\left[N\left\langle\begin{matrix}CO-CH_2\\ |\\ CO-CH_2\end{matrix}\right.\right]_2 + 2C_6H_5Br.$$

Comparing the dibenzyldiphenyltin reactions with those of benzylphenylmercury, we note the difference in the behavior of the phenyl and benzyl groups attached to mercury and to tin. In photo reactions, the benzyl group is the first to be split off from mercury, whereas it is more firmly attached to tin than the phenyl group is. In ionic reactions (such as the action of hydrogen chloride or succinimide), the process is the same for tin and mercury derivatives: the more highly electronegative phenyl radical is the first to be split off.

EXPERIMENTAL

Synthesis of Dibenzyldiphenyltin

A solution of 20 g of diphenyltin dichloride in 20 ml of ether was poured into an organomagnesium compound prepared from 8.5 g of magnesium, 44.3 g of benzyl chloride, and 150 ml of ether, and the reaction mixture was heated for one hour over a water bath. Then the solution was decomposed with ammonium chloride, and the ether layer was removed and desiccated with sodium sulfate. The oil left after the ether had been driven off was distilled with steam to eliminate byproducts of the reaction. The resultant product was dried in vacuum for 5-6 hours; it was an adequate amount of the substance, its yield being 24.2 g (or 92% of the theoretical).

Dibenzyldiphenyltin is a slightly yellowish, oily liquid.

d_{15}^{15} 1.271. 0.1610 g substance: 0.1270 g SnO_2. Found %: Sn 25.11. $C_{26}H_{24}Sn$. Computed %: Sn 26.01. 0.3606 g substance: 19.89 g benzene: Δt 0.230°. 0.9170 g substance: 18.80 g benzene: Δt 0.605°. Found: M 456.2, 447.1. $C_{26}H_{24}Sn$. Computed: M 451.5.

Photo Reactions of Diethyldiphenyltin

Reaction with chloroform. The reaction was carried out in sealed quartz test tubes 30-40 cm long and 1.5-2.0 cm in diameter. Radiation was supplied by a PRK-2 quartz lamp, 3.0 g of the substance being irradiated in 20 ml of chloroform for some 120 hours. An amorphous yellow powder totaling 0.07 g, which was insoluble in organic solvents, settled to the bottom of the test tube; it was not analyzed further. The chloroform was driven off from the filtrate, together with the benzene formed during the reaction. Nitration of the distillate yielded 0.36 g (or 24% of the theoretical) of m-dinitrobenzene, with a m.p. of 89°. A sample mixed with the pure substance exhibited no depression of the melting point. The residue left after the solvent had been driven off was distilled in vacuum. Two grams of a fraction boiling at 65-118° and 2 mm, which was a mixture of the unreacted substance, tetraethyltin, and diethyltin dichloride, was collected. The entire fraction was processed with an alcoholic solution of ammonia to recover the latter substance. This yielded 0.14 g of diethyltin oxide, which was analyzed for tin after it had been filtered out, washed, and dried.

0.1230 g substance: 0.07558 g SnO_2; found %: Sn 61.6. $C_4H_{10}SnO$. Computed %: Sn 61.4.

Titration of the filtrate after the ammonia treatment showed it to contain 0.0891 g of NH_4Cl, equivalent to 30.10% chlorine in the original substance in terms of the oxide synthesized; the calculated figure for $(C_2H_5)_2SnCl_2$ was 28.75%.

The residue left after the vacuum distillation yielded 0.13 g of crystals of triphenyltin chloride. The product had a m.p. of 106-110° after recrystallization.

Reaction with carbon tetrachloride. 30 g of the substance in 20 ml of the solvent was irradiated for some 140 hours. The insoluble, amorphous precipitate (0.14 g) was filtered out of the solution, and the solvent was driven off together with the chlorobenzene formed and then nitrated. Nitration yielded 0.22 g of chloronitrobenzene, with a m.p. of 81-82°. The residue left after the solvent had been driven off was distilled in vacuum, yielding 0.38 g of a solid product, with a m.p. of 68-72°, which proved to be diethyltin dichloride, plus easily sublimed crystals of hexachloroethane, with a m.p. of 178-179° in a sealed capillary. A sample mixed with the pure substance exhibited no depression. The diethyltin dichloride had a m.p. of 82° after recrystallization, diethyltin oxide being recovered from the alcoholic solution by adding ammonia.

A total of 0.11 g of crystals of triphenyltin chloride, with a m.p. of 110°, was recovered from the residue left after the vacuum distillation by recrystallization from acetone.

Reaction with methanol. 3 g of diethyldiphenyltin in 20 ml of methanol was irradiated for some 110 hours. A mirrorlike coating of metallic tin was observed on the walls of the test tube. The methanol was driven off and diluted with water. This caused benzene to separate out; the latter was nitrated, yielding 0.41 g of m-dinitrobenzene, with a m.p. of 89°. The aqueous-alcoholic solution contained formaldehyde, as was proved by reactions with resorcinol and by its silver mirror. The liquid products were distilled at 7-mm vacuum within the

115-130° range; they had a d_{15}^{15} 1.628. It is obvious that this was a mixture of the unreacted diethyldiphenyltin (*d* 1.588) and tetraethyltin (*d* 1.750). Analyzing this fraction for tin yielded similar figures.

0.3150 g substance: 0.1810 g SnO_2. Found %: Sn 45.1. $C_{16}H_{20}Sn$. Computed %: Sn 35.7. $C_8H_{20}Sn$. Computed %: Sn 50.4.

The residue left after vacuum distillation was a solid weighing 0.28 g that was insoluble in organic solvents. It was evidently the oxide of the diethyltin, since it dissolved extremely freely in alcoholic hydrochloric acid, yielding diethyltin dichloride, which was recovered as crystals with a m.p. of 81° that exhibited no depression of the melting point when mixed with the pure substance.

Photo Reactions of Dibenzyldiphenyltin

Reaction with chloroform. A solution of 3 g of dibenzyldiphenyltin in 15 ml of chloroform was irradiated for some 100 hours. The solvent was driven off and nitrated, yielding 0.33 g of *m*-dinitrobenzene with a m.p. of 89°. The residue left after the solvent had been driven off yielded 0.26 g of crystals of dibenzyltin dichloride, which had a m.p. of 163° after recrystallization from benzene. A sample exhibited no depression when mixed with the pure substance. After the dibenzyltin dichloride was filtered out, the liquid product was steam-distilled, but no dibenzyl was recovered. The residue left after the steam distillation was treated with benzene; driving off the latter left behind 2.0 g of the unreacted original substance. After the residue had been extracted with benzene there remained 0.40 g of dibenzyltin oxide, formed by hydrolysis of the chloride during the steam distillation. The oxide was dissolved in alcoholic hydrochloric acid, thus converting it into dibenzyltin dichloride (0.47 g), the latter thus totaling 0.73 g (or 30% of the theoretical).

Reaction with carbon tetrachloride. A solution of 3 g of dibenzyldiphenyltin in 15 ml of CCl_4 was irradiated for some 60 hours. The subsequent processing was the same as in the test with chloroform. We secured 0.22 g of chloronitrobenzene, 0.28 g of dibenzyltin dichloride, 0.45 g of dibenzyltin oxide, and 1.69 g of the unreacted substance.

0.1784 g substance: 0.0962 g SnO_2. Found %: Sn 42.43. $C_{26}H_{14}SnCl_2$. Computed %: Sn 42.60. 0.4000 g substance: 23.98 g benzene: Δt 0.22°. Found : M 371.7. $C_{26}H_{14}SnCl_2$. Computed: M 371.0.

Reaction of dibenzyldiphenyltin with an alcoholic solution of hydrogen chloride. 2.5 g of the substance was dissolved in 10 ml of an 0.86 *N* solution of hydrogen chloride. The solvent was driven off together with the resultant benzene, which was recovered by processing the distillate with water. Nitration yielded 0.25 g of *m*-dinitrobenzene with a m.p. of 89°. Crystals of dibenzyltin dichloride were recovered from the flask after the solvent had been driven off. Recrystallization yielded 1.6 g of the product, with a m.p. of 163°. The yield was 80% of the theoretical.

Reaction of dibenzyldiphenyltin with bromosuccinimide. 2.0 g of the substance dissolved in 10 ml of chloroform was heated with 1.56 g of N-bromosuccinimide for half an hour with a reflux condenser over a water bath. After the reaction, the chloroform and the bromobenzene were driven off, the latter being converted into dinitrobromobenzene by nitration. A total of 0.57 g of the latter was recovered, with a m.p. of 73°. The residue left after the solvent and the bromobenzene had been driven off was treated with hot water. Evaporation of the aqueous solution yielded 0.75 g of succinimide with a m.p. of 122°. The residue left after the water processing was dissolved in an alcoholic solution of hydrogen chloride; the solution yielded 0.49 g of dibenzyltin dichloride with a m.p. of 161°.

Reaction of dibenzyldiphenyltin with succinimide. 2 g of the substance was heated with 0.92 g of succinimide in a small flask over an oil bath to 170°. The mixture was oxidized with a solution of potassium permanganate. After oxidation, the benzene was driven off with steam and extracted with carbontetrachloride. Nitration of this mixture yielded 0.35 g of m-dinitrobenzene, with a m.p. of 89°. The aqueous solution was acidified, yielding 0.23 g of benzoic acid, which fused at 121°, and exhibited no depression of the melting point when mixed with the pure substance.

The residue in the flask was a solid that was insoluble in alcohol, ether, or benzene, though freely soluble in ethyl cellosolve. Recrystallization yielded 0.33 g of the substance. Processing an alcoholic solution of the substance with hydrogen chloride yielded two substances: dibenzyldichlorotin, with a m.p. of 163°, and diphenyldichlorotin, with a m.p. of 43°.

SUMMARY

1. A study has been made of the photochemical reactions of diethyldiphenyltin with carbon tetrachloride, chloroform, and methanol. In every instance the phenylgroup was split off, it then reacting further with the solvent.

2. A study was made of the reaction of dibenzyldiphenyltin with an alcoholic solution of hydrogen chloride and chloroform. Here again, the initial reaction is the detachment of the phenyl radical.

3. The reactinn of dibenzyldiphenyltin with an alcoholic solution of hydrogen chloride yielded benzene and dibenzyltin dichloride.

4. Heating dibenzyldiphenyltin with succinimide split off the phenyl and benzyl groups.

5. Bromosuccinimide split off the phenyl radical from dibenzyldiphenyltin, yielding bromobenzene.

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OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XVI. THE OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF 2,3-DIHYDROXY-1,4-NAPHTHOQUINONE AND 1,2,3,4-TETRAOXOTETRALIN

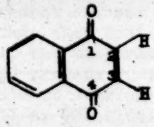
A. S. Khokhlov, L. A. Shchukina and M. M. Shemyakin

The present paper deals with the hydrolytic and oxidative-hydrolytic transformations of 2,3-dihydroxy-1,4-naphthoquinone (isonaphthazarine) (III) and the structurally similar 1,2,3,4-tetraoxotetralin (IV).

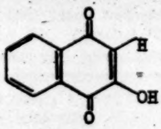
Isonaphthazarine (III) and the tetraketone (IV) are instances of highly oxidized carbocyclic compounds, about the cleavability of whose ring systems in the presence of oxidizing and hydrolyzing agents very little is known up to the present time. And yet these very substances can sometimes form less highly oxidized carbocyclic compounds as intermediate products of their oxidative-hydrolytic transformations,* so that learning the nature of the cleavages of isonaphthazarine (III) and the tetraketone (IV), and the conditions governing them, would contribute greatly to an explanation of such reactions in other carbocyclic compounds.

Research on these two compounds was also desirable with a view to the investigation of the relationships between the degree of oxidation of the carbocyclic compounds and the ability of the carbon bonds in their ring systems to undergo hydrolytic cleavage.

In a series of previous reports we have shown that the preliminary oxidation of the molecules usually facilitates subsequent hydrolytic cleavage of the carbon bonds. It should have been expected from theoretical considerations, however (cf. Par. 4, Report I [2]), that in some instances oxygen-containing substituents added to the molecule under the action of an oxidizing agent would not facilitate, but, on the contrary, would impede the cleavage of the bonds that were to undergo hydrolysis. In such cases, transformations of the given type can be effected only after further oxidation of the molecule. This problem naturally demanded special study, and isonaphthazarine (III) and the tetraketone (IV) were particularly suited for an experimental check of the correctness of this hypothesis.



(I)



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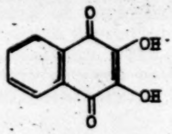

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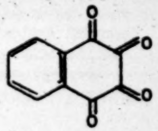

(IV)

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*Cf [1] and next report.

When we compare the structural formulas of 1,4-naphthoquinone (I), 3-hydroxy-1,4-naphthoquinone (II), isonaphthazarine (III), and the tetraketone (IV), we are led to assume that the successively greater oxidation of the 1,4-naphthoquinone molecule evident in this series will not always promote an increase in the ease with which the carbon bonds of the ring systems are ruptured.

It ought to be easier to cleave 3-hydroxy-1,4-naphthoquinone (II), an example of the first stage of oxidation of 1,4-naphthoquinone (I), than the latter compound, since the hydroxyl group in the 3 position strongly polarizes the bond between the 2 and 3 carbon atoms in the molecule of the hydroxynaphthoquinone as well as in its hydration product. Isonaphthazarine (III), which is an example of the second stage of oxidation of the initial quinone, ought to manifest much less of a tendency toward hydrolytic cleavage, however, because of the depolarization of the bond between the 2 and 3 carbon atoms due to the influence of the two hydroxyl groups attached to these carbon atoms. Only the further oxidation of the isonaphthazarine (III) to the tetraketone (IV) (which is the product of the third stage of oxidation of the 1,4-naphthoquinone) should again result in a marked facilitating of the hydrolytic cleavage of the ring system, inasmuch as the hydration of the carbonyl groups at the 2 and 3 positions in the tetraketone molecule ought to entail extremely strong polarization of the carbon bond between the 2 and 3 carbon atoms, due to the influence of the neighboring carbonyl groups.

Our researches have fully borne out these hypotheses. It has been shown previously [3,4] that 1,4-naphthoquinone (I) can be cleaved into phthalic and phthalonic acids merely by the simultaneous presence of the oxidant and the hydrolyzing agent, whereas 3-hydroxy-1,4-naphthoquinone (II) can readily undergo straight hydrolytic cleavage when boiled in aqueous buffer solutions with a pH approximating 7.5. Isonaphthazarine (III), however, proved to be highly resistant to hydrolytic agents – it suffers no change at all in aqueous alkaline solutions in the cold when no atmospheric oxygen is present, undergoing very slow oxidative-hydrolytic transformations, but no purely hydrolytic ones, when boiled. As for the tetraketone (IV), its ring system is cleaved hydrolytically with exceptional ease, as we might have expected; this process may be carried out, for example, by boiling an aqueous solution of the tetraketone (IV) for 20-30 minutes, while hydrolytic cleavage takes place practically instantaneously in an aqueous alkaline solution, even in the cold. Thus, the behavior of all these substances fully conforms to the patterns set forth above.

The behavior of isonaphthazarine (III) when simultaneously acted upon by an oxidant and hydrolytic agents is quite different. It then undergoes very thoroughgoing oxidative-hydrolytic cleavages, the nature and mechanism of which have remained quite unclear up to the present time, though Th. Zincke [5] noted long ago that isonaphthazarine in an aqueous alkaline solution is cleaved in the cold in the presence of atmospheric oxygen, yielding phthalonic acid and carbon dioxide.

A more detailed investigation of these reactions that was undertaken by the present authors has shown that transformations of this sort yield many more compounds than indicated by Th. Zincke, their nature depending on the pH of the medium, the temperature, and the presence of an oxidant. Thus, when the solution pH exceeds 7, the isonaphthazarine is rapidly cleaved by boiling in the presence of atmospheric oxygen,* yielding phthalidecarboxylic and phthalic acids as well as phthalonic acid and CO_2:

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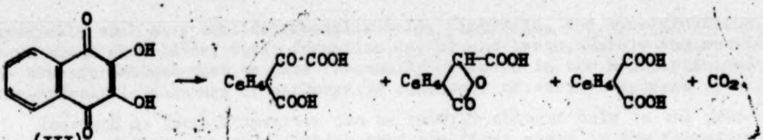
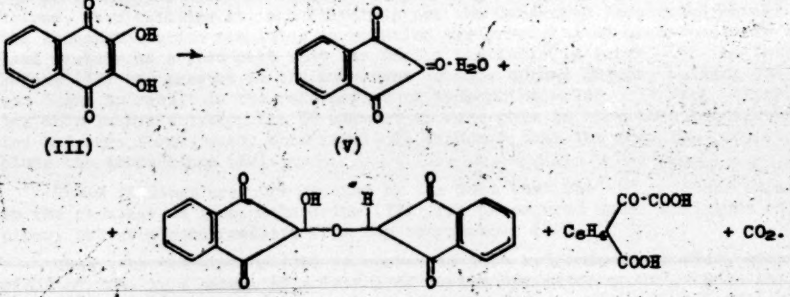
* When boiled in a 1% solution of caustic soda, for example, the reaction is complete within 30 minutes, provided the current of air passed through is strong enough.



(III)

The yield of phthalonic acid, which often exceeds 60%, depends but little upon the solution pH and the temperature at which the reaction is carried out. The formation of phthalidecarboxylic acid, however, requires a higher process temperature and a solution pH in excess of 7; under suitable conditions the yield of this acid may be as high as 20%. Phthalic acid is likewise formed at pH values above 7, though it is formed in rather considerable quantities (not exceeding 11%, however) even when the reaction is carried out in the cold.

When the aqueous isonaphthazarine solutions have an initial pH of 7, the compounds produced are altogether different. Boiling such a solution for a long time (24 hours) with atmospheric oxygen present yields neither phthalidecarboxylic acid nor phthalic acid, while the yield of phthalonic acid is halved (30%), but we do get very appreciable quantities of ninhydrin (V) (approximately 30%) and nearly 2% of hydrindanthine (VI).* In addition, about 1 mol of carbon dioxide is formed, together with as much as 8% of a neutral substance with a temp. decomp. of 247-249°, the empirical formula of which is $C_{20}H_{12}O_8$.



(III) (V)

(VI)

It is important to note that isonaphthazarine can be readily cleaved into the above-mentioned compounds only when atmospheric oxygen is present. It remains practically unchanged, for instance, when boiled in water or in a 1% aqueous solution of sulfuric acid for 24 hours. Nor does isonaphthazarine suffer practically any change when kept for 130 days in a 1% solution of caustic soda at 20° but with no atmospheric oxygen present. When this solution is boiled for 50 hours, about 15% of the isonaphthazarine is cleaved, to be sure, very small quantities of phthalidecarboxylic acid and traces of phthalic and phthalonic acids being found, but on the whole nothing but highly tarred substances are formed. Inasmuch as isonaphthazarine, like other quinones, is itself an oxidizing agent, the formation of these latter compounds is due to the fact that it is able to manifest a certain oxidizing action under these conditions (cf below).

At first glance, it would appear to be extremely difficult to trace all the paths leading to the formation of all these cleavage products of isonaphthazarine, especially such as phthalidecarboxylic acid, ninhydrin, and hydrindanthine. But, as we shall show later, their formation is, by and large, merely the result of the transformations that we have frequently observed in the hydrolytic and oxidative-hydrolytic cleavage of carbocyclic compounds of various degrees of oxidation.

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*The structure of hydrindanthine cannot be considered rigrously proved at the present time. [17]

Inasmuch as isonaphthazarine can be readily changed only in the presence of atmospheric oxygen, one should think that the first stage in the formation of all the end products mentioned above is the oxidation of the isonaphthazarine (III) to the tetraketone (IV), the structural features of which ought to make it extremely easy to hydrate and then to cleave hydrolytically.

We know that isonaphthazarine exhibits a pronounced tendency to be converted into the tetraketone (IV) in the presence of an oxidant [5]. The formation of the latter under the conditions in which the isonaphthazarine undergoes the transformations described above was therefore highly probable. Inasmuch as our findings indicated that the tetraketone (IV) is cleaved almost instantaneously in aqueous alkaline solutions, it could, of course, not be found when the reaction was carried out in an alkaline solution. Still, this compound is somewhat more stable in a boiling aqueous solution, in which it takes 20-30 minutes for it to decompose (cf below). We therefore might hope to detect it, even if only indirectly, by cleaving isonaphthazarine in an aqueous solution with an initial pH of 7. We succeeded in doing so by making use of the highly characteristic property of the tetraketone (IV) of being partially reconverted into isonaphthazarine (III) when boiled in an aqueous solution. This was done by conducting the cleavage of isonaphthazarine as follows: evaporating the reaction solution to small volume, then chilling it, and filtering out the unreacted isonaphthazarine. Then the isonaphthazarine remaining in solution was precipitated quantitatively with lead acetate as a lead salt that was wholly insoluble in water. If the tetraketone (IV) was present in the resultant aqueous mother liquor, boiling the latter ought to result in the reformation of isonaphthazarine. In fact, after boiling this latter solution for 30 minutes we were able to show that isonaphthazarine had been formed anew; this result is evidence that the reaction products include the tetraketone (IV).

These findings are corroborated by the fact that the end products formed in the cleavage of isonaphthazarine (III) can be secured under analogous conditions, but even more readily, from the tetraketone (IV). *

Thus, the tetraketone (IV) is converted into hydrindanthine (VI), with a yield of 20%, in a saturated solution of barium hydroxide at 20°. When the tetraketone (IV) is boiled for a short time in a 1% caustic soda solution with atmospheric oxygen present, it is rapidly cleaved into phthalonic and phthalidecarboxylic acids. Lastly, boiling it with water yields up to 45% of ninhydrin (V) and some 50% of carbonic acid within 20-30 minutes. ** This makes it fairly obvious that the first stage of the oxidative-hydrolytic transformations of isonaphthazarine (III) is its oxidation to the tetraketone (IV).

Let us now consider the subsequent steps in these transformations. It was highly probable that the further changes in the tetraketone (IV) largely involved the formation of ninhydrin (V), no matter how the initial isonaphthazarine or the tetraketone had been cleaved. As we shall show below, this supposition proved largely to be correct. We must first, however, deal with the problem of the ways in which the tetraketone is converted into ninhydrin, the yields of which are fairly high when aqueous solutions of isonaphthazarine or of the tetraketone are boiled, though it is not produced when the reaction is carried out in the presence of aqueous solutions of alkalies.

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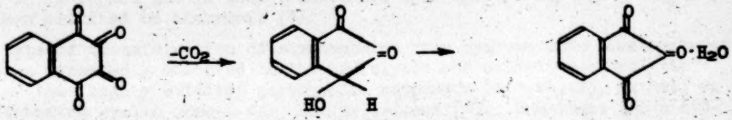
* With the exception of the compound with the empirical formula $C_{20}H_{12}O_8$, which can be secured only from isonaphthazarine.

** It should be noted that when the tetraketone (IV) is boiled with water, only about half of it is converted into ninhydrin and carbon dioxide, the other half being reduced to isonapthazarine. A similar reaction occurs when the crystalline dihydrate of this tetraketone is heated to 130° for 30 minutes. The reasons for these phenomena are discussed below.

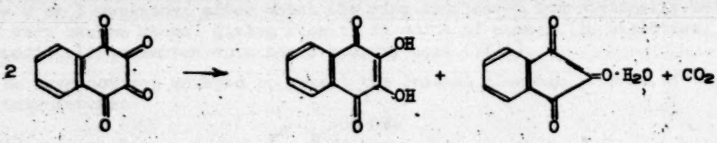
We know that triquinoyl (hydrated hexaketocyclohexane), an analog of the tetraketone (IV), readily evolves 1 mol of carbon dioxide when boiled with water, being thus converted into so-called croconic acid (tetraketocyclopentanol). The latter, in turn, can be readily oxidized to pentaketocyclopentane, the hydrated form of which has been termed "leuconic acid." The structure of this latter compound is somewhat like that of ninhydrin (V) [6]. Th. Zincke observed similar transformations in his study of the properties of some polyhalogenated cyclic mono-, di-, and triketones [7]. Several similar reactions have been described for some other types of carbocyclic compounds [2,4,8-12]. We could therefore conclude that when the tetraketone (IV) is boiled in water, a molecule of carbon dioxide is first split off, the respective hydroxy diketone (VII) being formed, which is then oxidized to ninhydrin (V):



(IV) (VII) (V)

We know from the literature [13] that the hydroxy diketone (VII) usually cannot be secured in the pure state because it is oxidized even by atmospheric oxygen, being converted either into ninhydrin (V) or hydrindanthine (VI). We recovered about 2% of the latter compound when we boiled isonaphthazarine (III) with water in the presence of atmospheric oxygen, carbon dioxide being split off at the same time and appreciable quantities of ninhydrin (V) being formed. Hydrindanthine (VI) can also be prepared from the tetraketone (IV), the yield being 20%, by reacting the latter at 20° with a saturated aqueous solution of barium hydroxide. Thus it is quite obvious that the formation of ninhydrin (V) from the tetraketone (IV) or from isonaphthazarine (III) precedes the splitting off of the molecule of carbon dioxide and the emergence of the hydroxy diketone (VII), which is readily recovered as hydrindanthine (VI).

Inasmuch as the hydroxy diketone (VII), which is highly reducing, is oxidized to ninhydrin (V) extraordinarily rapidly, while the tetraketone (IV), which is a fairly strong oxidizing agent, can be reduced to isonaphthazarine (III) rather easily, we can see why boiling an aqueous solution of the tetraketone converts the latter into nearly equal quantities of isonaphthazarine and ninhydrin while evolving about 50% of carbon dioxide, whereas no hydrindanthine is formed at all under these conditions:

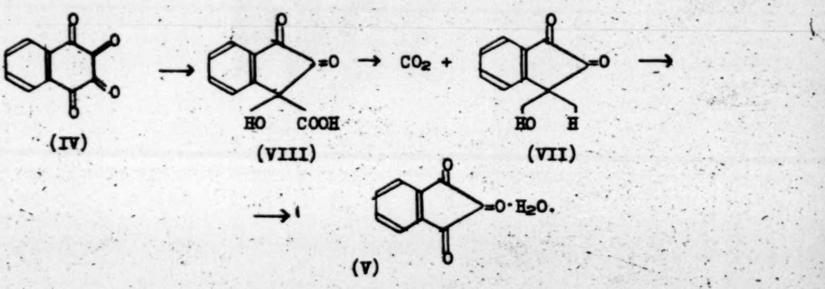


(IV) (III) (V)

The hydroxy diketone (VII), which appears as an intermediate product of the tetraketone (IV), is evidently oxidized to ninhydrin at the instant of its formation by the as yet unchanged tetraketone, which is reduced at the same time to isonaphthazarine (III). It is important to bear in mind at this point that practically equal quantities of isonaphthazarine and ninhydrin are secured by boiling an aqueous solution of the tetraketone whether atmospheric oxygen is present or not. Hence, in this stage it is the tetraketone (IV) rather than the atmospheric oxygen that is the oxidizing agent. It follows, therefore, that in the conversion of isonaphthazarine into ninhydrin the atmospheric oxygen is required solely to oxidize the original isonaphthazarine to the tetraketone (IV), the oxygen not taking part in the subsequent stages of the reaction.

Inasmuch as the foregoing facts leave no shadow of doubt that the tetraketone (IV) is converted into ninhydrin (V) via the hydroxy diketone (VII), let us now deal briefly with the manner in which the latter is formed from the original tetraketone. To judge from the numerous analogous instances described earlier, the first thing that apparently happens is the formation of a bicyclic α-hydroxy acid (VIII), which splits off its carboxyl group as a molecule of carbon dioxide as soon as it is formed and is thus transformed into the hydroxy diketone (VII), which is then oxidized to ninhydrin (V).

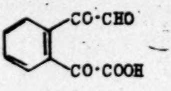
This type of transformation of six-membered ring systems into five-membered ones has been repeatedly observed in the hydrolytic and oxidative-hydrolytic cleavages of less highly oxidized carbocyclic compounds [2,8,11,12], as well as in polyhalogenated cyclic mono-, di-, and triketones [7]. Sometimes the α-hydroxy acids, such as the acid (VIII), can be isolated as such, but in most instances they undergo subsequent changes very easily, the most common one being decarboxylation. Since the acid (VIII) is a β,γ-diketo acid, it ought to be decarboxylated very easily, which is evidently why it can not be isolated when the reaction is carried out under the conditions set forth above.



(IV) (VIII) (VII) (V)

As for the manner in which the α-hydroxy acid (VIII) is formed, this apparently involves the initial hydration of the tetraketone (IV) at the carbonyl group at the 2 or 3 position, after which the ring is cleaved hydrolytically between these very carbon atoms, giving rise to an anion of monocyclic structure, which is immediately converted into the α-hydroxy acid (VIII).

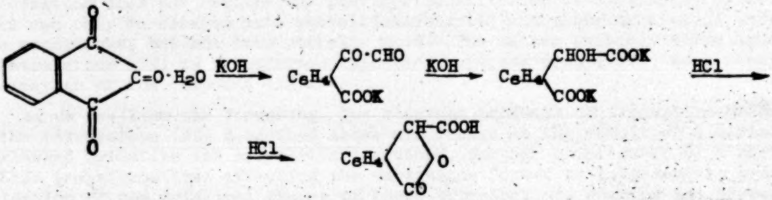
We have not yet managed to detect the initial cleavage product of the original tetraketone:



(IX)

evidently because compounds of this type must be highly unstable when the reaction medium contains both oxidizing and hydrolyzing agents. It is quite possible that some of the phthalonic and phthalic acids secured as the end products of the cleavage of isonaphthazarine arise as the result of the decomposition of the compound (IX) mentioned above. It should be emphasized, however, that much of the phthalonic acid, together with all the phthalidecarboxylic acid, is doubtless formed as the result of the subsequent transformations of the ninhydrin (V), which as a rule undergo thoroughgoing changes partially or completely during the cleavage of the original isonaphthazarine (III) or of the tetraketone (IV).

It is asserted in the literature [13] that when ninhydrin is acted upon by a 15% aqueous solution of caustic potash, it is first converted into a salt of o-carboxyphenylglyoxal and then into a salt of o-carboxyamygdalic acid, which turns into phthalidecarboxylic acid upon acidulation:



It has been found that similar transformations are possible in some of the halogenated ketones of indane series [14]. It was therefore quite probable that the phthalide-carboxylic acid we had found among the products of the oxidative-hydrolytic cleavage of isonaphthazarine (III) and of the tetraketone (IV) was formed as the result of the cleavage of the previously formed ninhydrin (V). This supposition seemed to be all the more likely since the phthalidecarboxylic acid was always secured whenever the process was carried out in alkaline rather than neutral solutions. We actually found that phthalidecarboxylic acid can be secured from ninhydrin, and with greater ease, under the same conditions as are used to cleave isonaphthazarine to produce the acid. Our results indicate, for example, that ninhydrin is converted into phthalidecarboxylic acid almost quantitatively within 2-3 minutes at 20° in the presence of a 1% solution of caustic soda, only traces of phthalonic acid being formed. This explains why ninhydrin is never found, and phthalidecarboxylic acid is always found, among the cleavage products of isonaphthazarine when the latter is cleaved in an alkaline medium. This clears up the manner in which phthalidecarboxylic acid is formed from isonaphthazarine.

Continuing our study of the properties of ninhydrin, we have found that it cannot be converted into phthalidecarboxylic acid when the solutinn pH is equal to or below 7. These findings were not unexpected, since it must be remembered that the o-carboxyphenylglyoxal formed as an intermediate product in one of the stages of the transformation of ninhydrin into phthalidecarboxylic acid must undergo an intramolecular Cannizaro reaction, which usually takes place only in an alkaline medium. That is why we never found any phthalidecarboxylic acid when we carried out the oxidative-hydrolytic cleavage of isonaphthazarine in neutral or acid solutions.

Though ninhydrin is not converted into phthalidecarboxylic acid when the solution pH equals or is less than 7, it does not remain altogether unchanged when such solutions are boiled for a long time. As in an alkaline medium, the ninhydrin can then be cleaved hydrolytically, though very slowly to be sure, the intermediate o-carboxyphenylglyoxal being oxidized at once by atmospheric oxygen or by the as yet unchanged ninhydrin and wholly converted into phthalonic acid. Thus, boiling a 0.1% aqueous solution of ninhydrin for 24 hours with atmospheric oxygen present yields about 12% phthalonic acid. No phthalic acid is formed under these conditions. These findings are in full agreement with the results of the oxidative-hydrolytic cleavage of isonaphthazarine by boiling its aqueous solution, with an initial pH of 7, in the presence of atmospheric oxygen, when we secured phthalonic acid together with hydrindanthine and ninhydrin, but no phthalidecarboxylic or phthalic acid (cf. below). It is now clear that at least part of the phthalonic acid formed during the cleavage of isonaphthazarine arises as a result of the decomposition of the ninhydrin.

As for the phthalic acid, small quantities of which are secured when isonaphthazarine is cleaved in aqueous alkaline solutions in the cold (cf. below), its formation does not require the previous constitution of ninhydrin, since the latter can only be cleaved into phthalidecarboxylic and phthalonic acids under these conditions, but not into phthalic acid. The latter probably forms when the tetraketone (IV) is transformed into the α-hydroxy acid (VIII) as a result of the cleavage of the compound (IX).

As we see from the foregoing, the cleavage products of isonaphthazarine (III) and the tetraketone (IV) described above are formed as the result of a series of interlinked oxidative and hydrolytic reactions, further complicated by a series of other transformations affecting the substances formed as intermediate products. Elucidation of the principal stages of these processes now enables us, however, to comprehend not only the reasons for the formation of the various end products, but also the ways in which they are formed. Notwithstanding the complexity and manysidedness of these transformations, they differ but little from the analogous reactions repeatedly observed in the past in the oxidative-hydrolytic or purely hydrolytic cleavage of six-membered ring compounds that are less highly oxidized than isonaphthazarine (III) or the tetraketone (IV).*

Similar transformations were also observed in several polyhalogenated six-membered cyclic mono-, di-, and triketones [7], as well as in triquinoyl [8]. In fact, most of these compounds display a marked tendency toward conversion into the respective five-membered carbocyclic compounds under given conditions. Hence, all these substances, notwithstanding their frequently great differences in structure, undergo similar changes, by and large, when oxidizing and hydrolyzing agents are present.

Ascertaining the channels and nature of the oxidative-hydrolytic cleavage of isonaphthazarine (III) and the tetraketone (IV) enables us to understand the mechanism of the formation of the end compounds that are formed during the simultaneous or alternative action of oxidizing and hydrolyzing agents upon other, less highly oxidized, carbocyclic compounds. It is therefore quite evident by now why boiling 1,4-naphthoquinone oxide with water for a long time yields appreciable quantities of ninhydrin, phthalonic acid, and hydrindanthine, in addition to isonaphthazarine (cf Report XV [1]).

We also understand the oxidative-hydrolytic transformations of substituted monohydroxy naphthoquinones, described in our next report, which can be cleaved into phthalic, phthalonic, and phthalidecarboxylic acids by boiling in an aqueous alkaline solution with atmospheric oxygen present. The latter compounds are formed because the original quinones are converted into the tetraketone (IV) during one of the intermediate stages.

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*See our previous reports (II-XV), dealing with oxidative-hydrolytic transformations of organic molecules, as well as the survey of the literature on the subject contained in Report I [2].

EXPERIMENTAL

1. Behavior of Isonaphthazarine When No Atmospheric Oxygen Is Present

a) When boiled in water. This experiment was run in a wide-necked flask, fitted with a reflux condenser and a tube reaching down to the bottom of the flask, through which a current of hydrogen, purified as described in Report XIV [4], (Experiment 1e) was passed throughout the run. There was a hole in the flask's stopper through which a tightly fitting glass rod passed, the rod terminating in a hook, to which a vessel containing 6 g of isonaphthazarine was attached before the start of the experiment.* The top of the condenser was connected to an absorption system, consisting of four Drexel bottles connected in series, each containing 50 ml of a titrated 1 N solution of sodium hydroxide, in order to absorb any carbon dioxide that might be formed during the run. The absorption system was connected at one end to the condenser and, at the other to two Tishchenko bottles containing an alkaline solution of pyrogallol, via two three-way stopcocks, which were interconnected by a glass tube. This made it possible to pass the current of gas from the flask either through the absorption system containing the titrated alkali solution or, by-passing it, directly to the Tishchenko bottles. Three liters of water were placed in the reaction flask, the airtightness of the system was checked, and the air was driven out of the flask through the by-pass tube. At the same time the water in the flask was heated to boiling. The air was driven out for two hours after boiling had set in, then the absorption system containing the titrated alkali solution was connected, and the air was driven out for another 2 hours. Then the vessel containing the isonaphthazarine was immersed in the water, and boiling was continued for another 24 hours. After the reaction solution had cooled off in a current of hydrogen, the alkali solution in the absorption system was back-titrated with acid, first against phenolphthalein, and then with methyl orange.

It was found that none of the alkali was consumed when the reaction was carried out under the conditions specified above, whence it follows that no carbon dioxide was split off in this case.

The reaction solution was evaporated to a volume of 150 ml in a hydrogen atmosphere, and the resulting precipitate was filtered out. This yielded 5.8 g of red crystals with a m.p. of 281°, which exhibited no depression of the melting point when mixed with isonaphthazarine. 10 ml of a 10% solution of lead acetate was added to the filtrate, and the blue precipitate of the lead salt of isonaphthazarine was filtered out. Decomposition of the resulting salt with 3 ml of a 5% solution of nitric acid yielded 0.15 g of isonaphthazarine. Practically all the isonaphthazarine (5.95 g, or 99%) was recovered.

b) When boiled in 1% H_2SO_4. After 6 g of isonaphthazarine had been boiled for 24 hours in 3 liters of a 1% aqueous solution of sulfuric acid under the conditions set forth for Experiment 1-a, 5.9 g (98%) of the isonaphthazarine was recovered.

c) In the presence of a 1% solution of NaOH at 20°. Four g of isonaphthazarine was dissolved in 500 ml of a 1% solution of sodium hydroxide that contained no dissolved oxygen. The solution was set aside to stand at 20° without allowing atmospheric oxygen to gain access to it. After 130 days had passed, the solution was acidulated with 50% sulfuric acid, and the precipitated isonaphthazarine was filtered out, washed with water, and dried. The wash waters were combined with the filtrate, and the solution pH was adjusted to a value of about 3.0, after which it was evaporated to dryness in a current of hydrogen at 40° in vacuum. The dry residue was extracted with ether in a Soxhlet apparatus. Practically all the isonaphthazarine (3.95 g; m.p. 280°) was recovered unchanged.

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* The isonaphthazarine was prepared by oxidizing 1,2-napthoquinone with a solution of calcium hypochlorite [5]. M.p. 282° (from acetic acid).

d) When boiled in 1% NaOH. This test was run in an apparatus consisting of two 10-liter wide-necked, round-bottomed flasks. The first flask (A) was fitted with a reflux condenser and two tubes extending to the bottom of the flask. The second flask (B) had a reflux condenser, a dropping funnel, and one tube reaching to the bottom of the flask. Flasks (A) and (B) were connected together via a three-way stopcock, which was connected to one of the tubes in Flask (A), the upper end of the condenser of Flask (A), and the tube of Flask (B). Hydrogen, purified by the method described in Report XIV [4] (Experiment 1-e), entered the system via the second tube in Flask (A). The system terminated in two Tishchenko bottles (filled with an alkaline solution of pyrogallol), which were connected to the upper end of the condenser of Flask (B).

25 g of isonaphthazarine was placed in Flask (B) and 8 liters of a 1% sodium hydroxide solution in Flask (A), and the system was checked for airtightness. Then we began to drive out the air with hydrogen, the three-way stopcock being turned so as to connect the upper end of the condenser on Flask (A) to the tube that passed down to the bottom of Flask (B). At the same time the alkali in Flask (A) was heated to boiling. Two hours after the alkali had begun to boil, the stopcock was carefully turned so as to cover the opening to which the condenser on Flask (A) was connected, and the air was driven out of the tube in Flask (A) by the alkali solution, which rose in the tube as high as the three-way stopcock. At this instant the three-way stopcock was returned to its original position, and hydrogen was passed through the system for another two hours. Then the heating of Flask (A) was stopped, the alkali was allowed to cool off, the three-way stopcock was turned so as to connect the tube in Flask (A) that was filled with alkali with the tube in Flask (B), and the alkali solution, freed of oxygen, was transferred to Flask (B). The isonaphthazarine dissolved rapidly, turning the solution dark blue. The solution was then boiled for 50 hours (without stopping the current of hydrogen) and allowed to cool off, after which the solution pH was adjusted to 6.5-7.0 by adding a previously determined amount of 50% sulfuric acid via the dropping funnel. Then the solution was evaporated to a volume of about 1 liter in a current of hydrogen and allowed to cool off, after which the resultant precipitate, consisting of a mixture of isonaphthazarine and silicic acid formed by the action of the alkali solution upon the surface of the glass flask, was filtered out. The precipitate was extracted 7 times with hot acetic acid to separate the isonaphthazarine. The acetic-acid extracts yielded 14.56 g of isonaphthazarine with a m.p. of 280-281° (from acetic acid) plus 0.95 g of black tar.

The aqueous reaction solution left after the isonaphthazarine and the silicic acid had been filtered out was acidulated with 50% sulfuric acid until the solution contained 10% H_2SO_4, and the precipitated isonaphthazarine was filtered out. This yielded another 6.1 g with a m.p. of 281-282° (from acetic acid). After the isonaphthazarine had been filtered out, the filtrate was extracted four times with chloroform. Driving off the chloroform left 0.5 g of a highly tarred substance, which was boiled with activated charcoal in water. The filtrate was extracted with chloroform, evaporation of which to small volume yielded 0.1 g of isonaphthazarine. Further evaporation to dryness yielded 0.25 g of crystals, which had a m.p. of 151-152° after double recrystallization from benzene and exhibited no depression of the melting point when mixed with phthalidecarboxylic acid (m.p. 152° [15]). The yield of the latter totaled 1.1%.

The acid reaction solution secured earlier was extracted six times with ether after it had been extracted with chloroform. The ether solution was desiccated with sodium sulfate, and the ether was driven off. This left 0.8 g of a highly tarred substance, which was boiled with 30 ml of water and activated charcoal. The filtrate was acidulated with 20 ml of 50% sulfuric acid and extracted three times with ether. The ether solution was desiccated with sodium sulfate, and the ether was driven off. This left a small quantity of crystals mixed with an oil. The crystals were washed out of the oil with a small quantity of ether. They were crystals of phthalic acid with a m.p. of 199-201° (from water). The ether-extracted oil was phthalonic acid, which was identified as its quinoxaline derivative [10,16]. Only minute quantities of phthalic and phthalonic acids could be isolated.

2. Oxidative-Hydrolytic Cleavage of Isonaphthazarine in the Presence of Atmospheric Oxygen

a) By boiling with water. The test was run in apparatus resembling that described in Experiment 1-a, but with air present. Three liters of water was poured into the flask, and 6 g of isonaphthazarine was placed in the vessel located above the surface of the water. The water was boiled for two hours in a current of air that had been freed of its carbon dioxide, passing it through the by-pass tube. Then the absorption system containing a titrated solution of sodium hydroxide was connected, the vessel containing the isonaphthazarine was immersed in the water, and boiling was continued for 24 hours. The reaction solution was cooled, and the alkali in the absorption system was back-titrated with 1 N sulfuric acid, first against phenolphthalein and then against methyl orange. The carbon dioxide evolved consumed 77.04 ml of the 1 N alkali solution, representing 1.69 g of carbon dioxide (1.2 moles of CO_2 per mole of isonaphthazarine).

The reaction mass was analyzed, and the compounds it contained were isolated, by the procedure described in the previous report [1] (Experiment 2-a). We obtained: 0.75 g (12.5%) isonaphthazarine; 0.45 g (8%) of a compound with the empirical formula of $C_{20}H_{12}O_6$; 0.1 g (2%) of hydrindanthine; 2.2 g (30%) of ketohydrindenophenazine; and 3.6 g (30%) of the o-phenylenediamine salt of the quinoxaline derivative of phthalonic acid.

b) In a buffer solution (pH 7.4) at 20°. 1.9 g of isonaphthazarine was placed in 250 ml of a phosphate buffer solution (pH 7.4; capacity 1/15 mol). A strong current of air, containing no carbon dioxide, was passed through the dark-purple solution at 20° for 50 hours. Then the solution was acidulated with 50% sulfuric acid, the percentage of H_2SO_4 in the solution being raised to 10%. This yielded 0.1 g (5%) of an isonaphthazarine precipitate, with a m.p. of 280-281° (from acetone and then from toluene).

The aqueous filtrate was repeatedly extracted with ether. The solvent was driven out of the ether solution, yielding 1.1 g of an oil that rapidly crystallized; the oil was heated in 2 ml of water until it dissolved and then allowed to stand overnight. 0.18 g (11%) of phthalic acid precipitated out. It was filtered out, the mother liquor left was strongly acidulated with 50% sulfuric acid, and the phthalonic acid extracted with ether. The acid was first refined by converting it into its lead salt and then by recrystallizing it from benzene and chloroform. This yielded 1.15 g (63%) of phthalonic acid with a m.p. of 143-144°.

c) In a NaOH solution at 20°. 1.9 g of isonaphthazarine was dissolved in 250 ml of 1 N sodium hydroxide, and a strong current of air, freed of its carbon dioxide, was passed through the resultant dark-blue solution at 20°. After 2-2.5 hours the reaction solution turned dark-yellow. It was extracted repeatedly with ether and then with chloroform (to remove the heavily tarred neutral substances), after which it was acidulated with 50% sulfuric acid until the percentage of H_2SO_4 in the solution was 10%, and then it was repeatedly extracted with ether. Driving off the solvent yielded 1.7 g of a tarred substance, from which 1.2 g of white crystals, a mixture of phthalic and phthalonic acids, was recovered by trituration with chloroform. They were separated as described in Experiment 2-b. This yielded 0.2 g (11%) of phthalic acid and 1.0 g of phthalonic acid. The chloroform mother liquor yielded another 0.3 g of phthalonic acid, the total yield of which was 1.3 g (66%).

The chloroform solutions contained, besides the phthalonic acid, about 0.2 g of tarry substances. No phthalidecarboxylic acid was found among the reaction products.

d) By boiling in a buffer solution (pH 7.4). Four liters of a phosphate buffer solution (pH 7.4; capacity 1/5 mol) was placed in a round-bottomed flask fitted with a reflux condenser and a tube extending to the bottom of the flask, through which air was passed throughout the experiment. The solution was brought to a boil, and 5.08 g of isonaphthazarine was added. The resultant solution was boiled for 32 hours with a strong current of air that had been freed of carbon dioxide always passing through. Then the solution was evaporated to 250 ml and acidulated with 50% sulfuric acid until the solution contained 10% H_2SO_4. 0.13 g (2.5%) of isonaphthazarine, with a m.p. of 280-281° (from acetone and then from toluene), precipitated out.

The reaction solution was repeatedly extracted with ether. Driving off the solvent left behind a highly tarred mass, which was triturated with chloroform several times. The chloroform solution was separated from the crystals, which were a mixture of phthalic and phthalonic acids. Separating this mixture as described in Experiment 2-b yielded 0.13 g (3%) of phthalic acid and 3.07 g (59%) of phthalonic acid.

Boiling the chloroform solution with activated charcoal and then driving off the solvent yielded 0.9 g (19%) of phthalidecarboxylic acid with a m.p. of 151-152° (from benzene).

e) By boiling in 1% NaOH. This experiment was carried out like Experiment 2-d. 5.7 g of isonaphthazarine was dissolved in 3 liters of 1% sodium hydroxide solution. The resultant blue solution was boiled while a strong current of air, freed of carbon dioxide, was passed through it. The solution turned dark yellow 30 to 45 minutes after boiling set in. It was acidulated with 50% sulfuric acid until its pH approximated 6.5 and then evaporated to a volume of 1 liter; its pH was again adjusted to 6.5, and it was re-evaporated to a volume of 300 ml. The cooled solution was acidulated with 50% sulfuric acid until its percentage of H_2SO_4 was 10%, and then extracted eight times with ether. The ether solution was processed as described in Experiment 2-d. This yielded: 3.8 g (65%) of phthalonic acid and 0.55 g (10%) of phthalidecarboxylic acid. No phthalic acid was found among the reaction products.

f) Proof of the formation of the tetraketone (IV) when isonaphthazarine is boiled in water. 4 g of isonaphthazarine was placed in 2 liters of water and boiled in an open flask while a strong current of air was passed through the reaction solution. After 6 hours of boiling the reaction mass had been reduced to a volume of 150 ml. A considerable amount of isonaphthazarine remained at the bottom of the flask throughout this time. The solution was cooled in a strong current of air, and the deposit of isonaphthazarine was filtered out. The isonaphthazarine left in the solution was precipitated completely with several batches of 2% lead acetate, the last batch being added until no more of the initially blue, and later light-blue, precipitate was thrown down. The subsequent addition of a few drops of the lead acetate solution produced a slight white turbidity, which dissolved upon shaking. The resultant solution, containing no isonaphthazarine,* was heated to a boil. A blue precipitate started to form almost immediately, gradually increasing in quantity. The boiling was stopped after 30 minutes, the solution was cooled, and a few more drops of lead acetate was added to it. The blue precipitate was filtered out, washed with water, and dried. Weight: 0.22 g. Decomposing it with sulfuric acid yielded 0.07 g of isonaphthazarine, with a m.p. of 280° (from alcohol), equivalent to about 0.18 g of the tetraketone (IV) present in the solution (cf Experiments 3-a and 3-c.

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* Preliminary tests had shown that isonaphthazrine can be precipitated quantitatively from aqueous solutions as its lead salt, which is practically insoluble in water.

3. Oxidative-Hydrolytic Cleavage of 1,2,3,4-Tetraoxotetralin (Tetraketone) (IV)

a) By boiling in water with atmospheric oxygen present. The experiment was carried out in apparatus resembling that described in Experiment 2-a, but in a half-liter flask. 400 ml of water was poured into the flask, and 4.5 g of the tetraketone (IV) dihydrate was placed in the vessel above the surface of the water.* The water was boiled in a current of air freed of its carbon dioxide, which passed out of the flask through a by-pass tube. After 1 hour of this boiling, the absorption system was connected, containing 200 ml of a titrated 0.5 N solution of sodium hydroxide, the vessel containing the tetraketone dihydrate was immersed in the water, and boiling was continued for one hour. After the reaction solution had cooled, the alkali in the absorbing bottles was back-titrated with a 0.5 N solution of hydrochloric acid, first against phenolphthalein and then against methyl orange.

The carbon dioxide evolved consumed 21.28 ml of the 0.5 N sodium hydroxide solution, equivalent to 0.468 g of carbonic acid. The yield of the latter was 52.8%.

Chilling the aqueous solution precipitated 1.6 g of isonaphthazarine with a m.p. of 280-281°. The isonaphthazarine remaining in solution was precipitated with lead acetate as its lead salt, decomposition of the latter with 5% nitric acid yielding 0.12 g of isonaphthazarine. The overall yield of the latter was 1.72 g (45%).

After the lead salt of isonaphthazarine had been filtered out, the mother liquor was evaporated in vacuum to a volume of about 10 ml, boiled with activated charcoal, filtered, and allowed to stand overnight. Crystals of ninhydrin, with a temp. decomp. of 239-240° (from water), settled out. Yield: 1.56 g (44%).

b) By boiling in water with no atmospheric oxygen present. This experiment was carried out in an atmosphere of hydrogen in an apparatus similar to that described in Report XIV [4] (Experiment 1-e). 300 ml of water was poured into the flask, while the vessel located above the surface of the water contained 3 g of the tetraketone dihydrate. After the air had been driven out, the vessel with the substance was immersed in the boiling water, and the solution was boiled for 30 minutes, cooled in a current of hydrogen, and then processed as described in Experiment 3-a. This yielded 1.2 g (47%) of isonaphthazarine and 1.14 g (48%) of ninhydrin.

c) Investigation of the rate at which the tetraketone (IV) is cleaved by boiling in water. The time required for the complete cleavage of the tetraketone hydrolytically was determined by the quantity of isonaphthazarine formed.

The experiment was run as follows: 100 ml of water was heated to boiling in a 200-ml round-bottomed flask, fitted with a reflux condenser and a tube reaching down to the bottom of the flask, through which air freed from carbon dioxide passed. 1 g of the tetraketone dihydrate was placed in the flask, and the solution was boiled for a certain time. The quantity of isonaphthazarine formed was determined as set forth in Experiment 3-a. The test results are tabulated in the adjoining table.

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* The tetraketone (IV) dihydrate, produced by oxidizing isonaphthazarine with nitric acid and chlorine [5], can be readily purified by recrystallizing it from ethyl acetate. This refining yields snow-white prismatic crystals with a temp. decomp. of 130-131° (cf Experiment 3g).

Test No.	Boiling time, min.	Isonaphthazarine yield		
		Grams	Per cent of theory	Per cent of the quantity secured after 60 minutes
1	2	0.15	17	37
2	5	0.25	29	63
3	10	0.27	32	70
4	30	0.37	44	95
5	60	0.39	46	100
6	120	0.39	46	100

d) Investigation of the rate at which the tetraketone is cleaved in a NaOH solution at 20°. Preliminary tests had shown that the tetraketone is precipitated very rapidly and nearly quantitatively by o-phenylenediamine from an aqueous solution with a pH of 3, the naphthodiphenazine formed in this reaction (m.p. 324-325° from acetic acid) being practically insoluble in water. We employed this reaction to determine the tetraketone in an aqueous solution.

The tetraketone was cleaved hydrolytically at 20° with an approximately 4% aqueous solution of sodium hydroxide. The latter solution was so prepared that mixing it with an equal volume of 1 N sulfuric acid would yield a solution whose pH would be about 3.0. The following solutions were also prepared in advance: a 2% aqueous solution of the tetraketone dihydrate; a 3% aqueous solution of o-phenylenediamine; and a 1 N solution of sulfuric acid.

Test 1. 10 ml of the sodium hydroxide solution was added to 10 ml of the tetraketone dihydrate solution; the solution turned dark blue. 10 seconds later 10 ml of the sulfuric acid solution was added, followed by 10 ml of the o-phenylenediamine solution. The precipitated naphthodiphenazine was filtered out, washed with water and dried. Weight: 0.01 g. Yield: 3%.

Test 2. This test was run like the preceding one, but the sulfuric acid solution was added after 15 seconds had elapsed. No naphthodiphenazine precipitate was formed at all after the solution of o-phenylenediamine had been poured in. Hence, the original tetraketone had been completely cleaved during this interval of time.

e) Cleavage of the tetraketone (IV) in a $Ba(OH)_2$ solution at 20°. To 1 g of the tetraketone dihydrate dissolved in 20 ml of water there was added 100 ml of a saturated aqueous solution of barium hydroxide. A dark-blue precipitate was thrown down. Hydrochloric acid was immediately added to the reaction mixture until the latter's reaction to Congo red was strongly acid. A white precipitate of hydrindanthine gradually settled out of the resulting orange solution. Yield: 0.15 g (19%). The substance fused at 229-230° after two or three recrystallizations from acetone and exhibited no depression of the melting point when mixed with hydrindanthine produced by reducing ninhydrin [13].

f) By boiling with 1% NaOH. This experiment was similar to the Experiment 2-d described above, 1.5 g of the tetraketone dihydrate being placed in 400 ml of a boiling 1% solution of sodium hydroxide. The resultant dark-blue solution was boiled while a strong current of air freed from carbon dioxide was passed through it. The solution turned yellow after 15 to 20 minutes; it was cooled and processed as in Experiment 2 d. We found: 0.9 g (69%) of phthalonic acid and 0.28 g (23.5%) of phthalidecarboxylic acid. No phthalic acid was found among the reaction products.

g) Thermal decomposition of the tetraketone (IV). 1 g of the tetraketone dihydrate was heated in a test tube fitted with an outlet tube, the end of which was immersed in a solution of barium hydroxide. The substance melted at 129-131°, turning red and evolving carbon dioxide. It was heated to 129-131° for 20 minutes. After it had cooled the reaction mass was triturated with 10 ml of cold water, and the undissolved isonaphthazarine was filtered out and triturated two more times with a small quantity of water. This left 0.3 g (35%) of isonaphthazarine with a m.p. of 281-282° (from alcohol).

The isonaphthazarine in the aqueous solution was precipitated as its lead salt by lead acetate; filtering out the salt left a colorless filtrate. A solution of 0.3 g of o-phenylenediamine in 5 ml of water was added to the latter. 0.38 g of ketohydrindenophenazine (m.p. 220° [13] from alcohol), was precipitated out, equivalent to 0.29 g (36.5%) of ninhydrin.

4. Hydrolytic Cleavage of Ninhydrin

a) By boiling in water with atmospheric oxygen present. A solution of 2 g of ninhydrin in 2 liters of water was boiled in a current of air for 24 hours, after which it was evaporated in vacuum to a volume of approximately 50 ml and chilled. 0.02 g of a tarry precipitate was thrown down. The filtrate was evaporated to a volume of approximately 15 ml and allowed to stand overnight. 1.12 g of ninhydrin settled out. A solution of 1 g of o-phenylenediamine in 10 ml of water was added to the filtrate. This precipitated 0.74 g of ketohydrindenophenazine, with a m.p. of 220° (from alcohol), equivalent to 0.57 g of ninhydrin. After the ketohydrindenophenazine had been filtered out, the filtrate was processed as described in Report XI [16], yielding 0.37 g of the quinoxaline derivative of phthalonic acid, with a m.p. of 240° (from alcohol), equivalent to 0.27 g (12.3%) of phthalonic acid.

b) By boiling in water with no atmospheric oxygen present. This experiment was carried out in an atmosphere of carbon dioxide in apparatus similar to that described in Report XIV [4] (Experiment 1-e). Two liters of water were placed in the flask, with 2 g of ninhydrin placed in the vessel located above the surface of the water. After the air had been driven out, the vessel containing the ninhydrin was immersed in the boiling water, and the ninhydrin solution was boiled for 24 hours in the current of carbon dioxide. The solution turned cloudy as the boiling approached its close. It was evaporated in a carbon dioxide current in vacuum to a volume of some 100 ml. The dark precipitate was filtered out and washed with water. Weight: 0.03 g. The filtrate was evaporated to a volume of about 15 ml and processed as specified in Experiment 4-a. This yielded 0.85 g of ninhydrin and 1.15 g of ketohydrindenophenazine (equivalent to 0.88 g of ninhydrin). A total of 1.73 g (86.5%) of ninhydrin was recovered. In addition we secured 0.13 g of the quinoxaline derivative of phthalonic acid, equivalent to 0.09 g (4.5%) of phthalonic acid.

c) By boiling in a H_2SO_4 solution. A solution of 2 g of ninhydrin in 2 liters of an 0.005 N solution of sulfuric acid (pH approximately 2.5) was boiled in a current of air for 24 hours. 10 ml of a 1 N solution of sodium hydroxide was cautiously added to the solution, with vigorous shaking. Subsequent processing was the same as in Experiment 4-b.

This yielded 0.65 g of ninhydrin, and 1.62 g of ketohydrindenophenazine (equivalent to 1.24 g of ninhydrin). A total of 1.89 g (94.5%) of ninhydrin was recovered. In addition, we secured 0.13 g of the quinoxaline derivative of phthalonic acid, equivalent to 0.09 g (4.5%) of phthalonic acid.

d) In a 1% NaOH solution at 20°. An approximately 2% aqueous solution of sodium hydroxide was prepared so as to yield a solution with a pH of approximately 3.0 when 10 ml of this solution was mixed with 5 ml of a 1 N sulfuric acid solution. We also prepared a 2% aqueous solution of ninhydrin and a 3% aqueous solution of o-phenylenediamine.

Test 1. 10 ml of the ninhydrin solution was added to 10 ml of the sodium hydroxide solution. The solution turned yellow, then green, then blue, and finally became colorless. After five minutes had elapsed, 5 ml of the sulfuric acid solution was added, followed by 10 ml of the o-phenylenediamine solution. No ketohydrindenophenazine was precipitated. The next day the solution was acidulated with 50% sulfuric acid until the percentage of H_2SO_4 in the solution was 10%, and then it was extracted eight times with chloroform. Driving off the chloroform yielded 0.16 g of phthalidecarboxylic acid, with a m.p. of 152° (from benzene). The aqueous mother liquor left after the chloroform extraction was extracted four times with ether. The ether extract was desiccated with sodium sulfate, and the ether was driven off. The residue of 0.04 g of yellowish crystals was triturated with a small quantity of warm chloroform, most of the substance dissolving. Driving off the chloroform yielded about 0.03 g of phthalidecarboxylic acid. The crystals that did not dissolve in the chloroform (weighing less than 0.01 g) were the quinoxaline derivative of phthalonic acid [16]. A total of 0.19 g (95%) of phthalidecarboxylic acid plus traces of phthalonic acid was secured.

Test 2. This test was similar to Test 1, the sulfuric acid being added after 3 minutes had elapsed. No ketohydrindenophenazine was precipitated after the solution of o-phenylenediamine had been added, though a slight cloudiness developed when the solution was allowed to stand overnight. The cloudiness was filtered out, and the solution was processed as in Test 1. This yielded 0.19 g (95%) of phthalidecarboxylic acid.

Test 3. This test was similar to Test 1, with the sulfuric acid being added after 1 minute had elapsed. After the solution of o-phenylenediamine had been added, a yellow precipitate of ketohydrindenophenazine settled out rapidly (m.p. 220°, from alcohol [13]); this was filtered out, washed with water, and dried. Weight: 0.13 g, equivalent to 0.1 g (50%) of ninhydrin. Processing the mother liquor as specified in Test 1 yielded 0.08 g (40%) of phthalidecarboxylic acid with a m.p. of 152° (from benzene).

SUMMARY

A study has been made of the nature, mechanism, and conditions governing the hydrolytic and oxidative-hydrolytic transformations of 2,3-dihydroxy-1,4-naphthoquinone (isonaphthazarine) and of 1,2,3,4-tetraoxotetralin. It has been shown that these two compounds can undergo a series of alternating oxidative and hydrolytic reactions in the presence of oxidizing and hydrolyzing agents, which are further complicated by other transformations of the substances formed as intermediate products. The principal stages of processes of this type have been ascertained, as well as their dependence upon the medium's pH and temperature, and upon the presence of oxidants.

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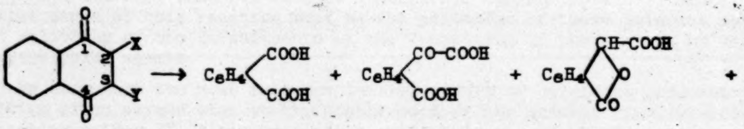
OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XVII. THE OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF SUBSTITUTED HYDROXYNAPHTHOQUINONES

D. P. Vitkovsky and M. M. Shemyakin

In studying the hydrolytic and oxidative-hydrolytic transformations of 3-hydroxynaphthoquinones that contain a hydroxyl group, a chlorine atom, an amino group, or a pyridinium group at the 2 position [Formulas (I) – (IV)], we found that when theyare boiled for a long time in an aqueous alkaline solution with atmospheric oxygen present, they all undergo a wholly monotypic cleavage (together with other changes), the course of which is independent of the nature of the substituents in the molecules. Under these conditions the substituents located at the 2-position are split off from the enumerated hydroxyquinones, while their rings are cleaved, yielding phthalic, phthalonic, and phthalidecarboxylic acids:



+ $HCl(NH_3, NC_5H_5)$

$X = OH$; $Y = OH$ (I)
$X = Cl$; $Y = OH$ (II)
$X = NH_2$; $Y = OH$ (III)
$X = \overset{+}{N}C_5H_5$; $Y = O^-$ (IV)

Inasmuch as these transformations are of an oxidative-hydrolytic nature, and the simultaneous action of oxidants and hydrolyzing agents upon carbocyclic compounds often results in the formation of phthalic and phthalonic acids (see, for example, [1-8]), the presence of the latter among the reaction products was rather natural. The formation of phthalidecarboxylic acid, however, seemed at first glance to be quite unexpected, since its formation, which requires the presence of an oxidant, is accompanied by the reduction of one of the carbonyl groups of the original quinone to a secondary alcohol group.

It might have been supposed that the first stage of the reaction we have discovered would be the transformation of the 3-hydroxynaphthoquinones that contain a chlorine atom, an amino group, or a pyridine radical at the 2-position into 2,3-dihydroxy-1,4-naphthoquinone (isonaphthazarine) (I), which would then undergo further changes under the action of the atmospheric oxygen and the aqueous solution of the alkali:

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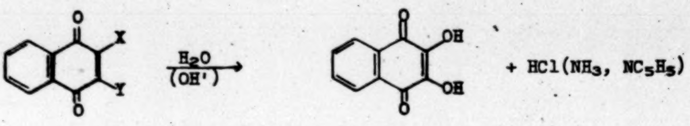

(I)

$X = O$; $Y = OH$ (II)
$X = NH_2$; $Y = OH$ (III)
$X = \overset{+}{N}C_5H_5$; $Y = O^-$ (IV)

This assumption might be based upon the following observations: 1) the splitting off of the enumerated substituents during the reaction as hydrogen chloride, ammonia, or pyridine; 2) the ability of 2-chloro-3-hydroxy-1,4-naphthoquinone (II) to form isonaphthazarine with a yield in excess of 50% when it is boiled in an aqueous alkaline solution with no atmospheric oxygen present; and 3) the ability of isonaphthazarine (I) to be cleaved very easily into phthalic, phthalonic, and phthalidecarboxylic acids when boiled in aqueous alkaline solution with atmospheric oxygen present [8].

But notwithstanding all these facts, our subsequent research has shown that the supposition advanced above was incorrect. We found that the two quinones, 2-amino-3-hydroxy-1,4-naphthoquinone (III) and the 2-pyridinium-3(1)-hydroxy-1,4(3,4)-naphthoquinone betaine (IV), in contrast to 2-chloro-3-hydroxy-1,4-naphthoquinone (II), cannot be transformed into either isonaphthazarine (I) or into the end products, phthalonic and phthalidecarboxylic acids, by boiling in an aqueous alkaline solution with no atmospheric oxygen present.* Hence, the initial stage of this reaction must be the oxidation of these quinones rather that splitting of the substituents at the 2-position of their rings by the action of hydrolyzing agents.

We know that the most frequent initial result of oxidizing quinones is the addition of an oxygen atom at the double bond of the quinone ring, yielding the respective oxides.** It has been often noticed (*e.g.*, *cf* [5,8]), on the other hand, that oxides of the quinones tend very much to be hydrated when they are heated in aqueous solutions of alkalines, turning into glycols. It may, therefore, be concluded that the oxidative-hydrolytic transformations of the hydroxy-naphthoquinones (I) – (IV) should involve, above all, their oxidation by atmospheric oxygen to oxides of the general type (V), which are then hydrated by the alkali solution to compounds of the general formula (VI), derivatives of 1,2,3,4-tetraoxotetralin. The latter are unstable, of course, in a boiling alkali solution; it is apparently in this stage that the substituents attached to the 2 carbon atom are split off as hydrogen chloride, ammonia, or pyridine, yielding the tetraketone (VII) (more precisely, its hydrate), which is then converted into phthalic, phthalonic, and phthalidecarboxylic acids:

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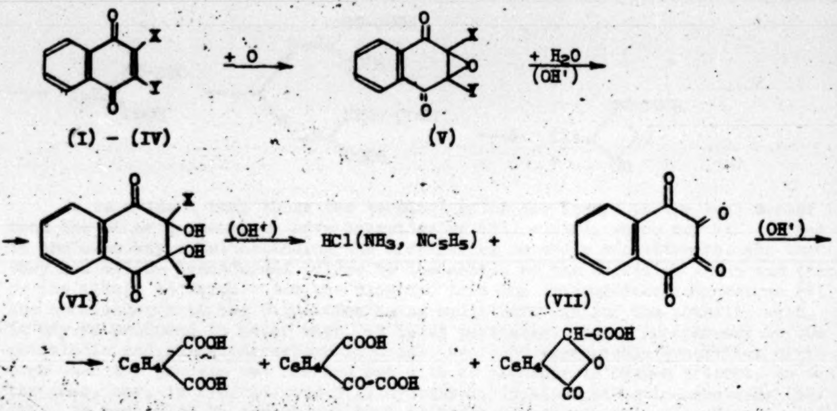
* Under these conditions the 2-pyridinium-3(1)-hydroxy-1,4,(3,4)-naphthoquinone (IV) yields 1-hydroxy-4-carboxyisoquinoline, pyridine and phthalic acid [2]. As for 2-amino-3-hydroxy-1,4-naphthoquinone (III), which we investigated in the form of its N-benzoyl derivative, it suffers but little change, owing to its structural peculiarities, even after 50 hours of boiling in a 1% solution of alkali. All we observed was the evolution of a slight amount of ammonia and the formation of small amounts of tarry substances; no individual products of the cleavage of the ring system of this quinone were detected (cf the experimental section of this paper).

** See [7] for a survey of the literature on this subject.



(I) - (IV)

(V)

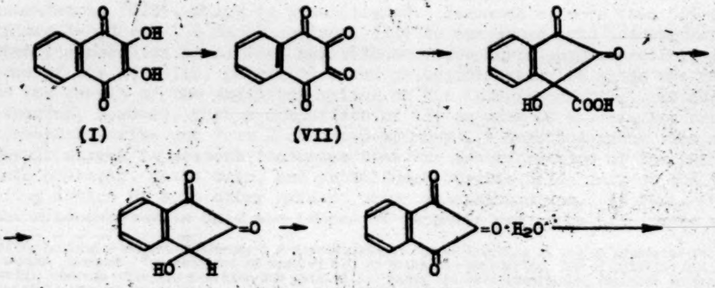
(VI)

(VII)

X = OH; Y = OH
X = Cl; Y = OH
X = NH_2; Y = OH
X = $\overset{+}{N}C_5H_5$; Y = O^-

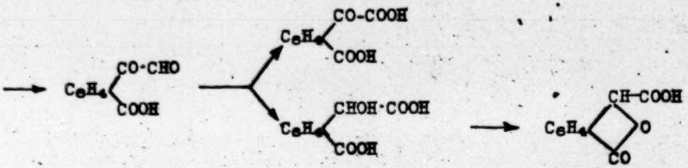
The last stage of this reaction - the cleavage of the tetraketone (VII) to the enumerated final acids - has recently been dealt with in a special study [e], in which it was found that this tetraketone can yield phthalonic and phthalidecarboxylic acids under the conditions in which it is produced from the substituted hydroxynaphthoquinones we have been investigating. On the other hand, it has been shown - in connection with one of these quinones; isonaphthazarine (I) [e] - that it is converted into the terminal acids only after it has been oxidized to the tetraketnne (VII). These facts, together with those set forth above, are weighty evidence in support of the reaction we have proposed.

As was learned in our previous report [e], the conversion of isonaphthazarine (I) into phthalonic and phthalidecarboxylic acids takes place via the following intermediate stages:



(I)

(VII)



It is evident that these two terminal acids are formed in the same manner from the other quinones we have investigated (II) - (IV), which are all cleaved in the same way notwithstanding the differences in their substituents, and that they can all be transformed (first by the action of the oxidizing agent and then by the alkali solution - see the diagram) into the intermediate tetraketone (VII), the substituents at the 2-position being split off. As for the phthalic acid, it may be produced in other ways, at least partially, since, in contrast to the phthalonic and phthalidecarboxylic acids, we found appreciable quantities of it even when the process was carried out with no atmospheric oxygen present, as was the case, say, in 2-pyridinium-3(1)-hydroxy-1,4(3,4)-naphthoquinonebetaine (IV) [2]. It must also be remembered that in this quinone the foregoing reaction is accompanied by other processes, which result in the formation of pyridine and of 1-hydroxy-4-carboxyisoquinoline (*cf* [2] for the way in which the latter compound is formed).

The transformations of isonaphthazarine (I) and 2-chloro-3-hydroxy-1,4-naphthoquinone (II) when they are boiled in an aqueous solution of alkali with no atmospheric oxygen present require special attention. In contrast to 2-pyridinium-3(1)-hydroxy-1,4(3,4)-naphthoquinonebetaine (IV) and 2-amino-3-hydroxy-1,4-naphthoquinone (III), which cannot be cleaved into phthalonic and phthalidecarboxylic acids under such conditions, as has been pointed out earlier, isonaphthazarine and 2-chloro-3-hydroxy-1,4-naphthoquinone can be converted into these acids as well as into phthalic acid whether atmospheric oxygen is present or not. In the latter case, to be sure, the yield of all of these acids is negligible, a fairly large quantity of tarry substances being produced.[*]

This circumstance seems to contradict the diagram proposed above, according to which the process can take place only when an oxidizing agent is present; it has been shown previously, however, that in the case of isonaphthazarine (I) [6], this is due to the high oxidizing ability of that quinone. That is why the latter displays oxidative action by itself, being partially auto-oxidized to the tetraketone (VII), which is then cleaved. Inasmuch as more than 50% of the 2-chloro-3-hydroxy-1,4-naphthoquinone (II) is converted into isonaphthazarine (I) when the reaction is carried out with no atmospheric oxygen present, at least some of the phthalic, phthalonic, and phthalidecarboxylic acids are then formed as the result of the oxidizing action of the isonaphthazarine. It must be stressed, however, that a comparison of the amounts of these acids produced from isonaphthazarine and from 2-chloro-3-hydroxy-1,4-naphthoquinone when no atmospheric oxygen is present indicates that the transformation of the latter quinone into phthalic, phthalonic, and phthalidecarboxylic acids must be due to the oxidizing action of some other oxidant than isonaphthazarine. In fact, about 1% of phthalidecarboxylic acid and traces of phthalic and phthalonic acids are formed after isonaphthazarine has been boiled for 48 hours in a 1% solution of sodium hydroxide [6], whereas 2-chloro-3-hydroxy-1,4-naphthoquinone yields 14% of phthalidecarboxylic, about 2.5% of phthalic, and about 1% of phthalonic acids. In the latter case, the role of oxidizing agent is taken over either by the original 2-chloro-3-hydroxy-1,4-naphthoquinone (in addition to the isonaphthazarine) or by one of the intermediate substances arising as the result of the quinone's subsequent transformations; we have isolated indanone-1-carboxylic acid-(3) (VIII) as the reduction end product, its yield being 18% when the reaction was carried out with no atmospheric oxygen present, whereas it is not formed at all in the presence of the latter. It is also worthy of note that the yield of indanone-1-carboxylic acid-(3) is nearly equivalent to the aggregate yield of phthalic, phthalonic, and phthalidecarboxylic acids, as a rule. It is therefore fairly obvious that when the reaction is carried out with no atmospheric oxygen present, these acids can be formed only as the result of the presence of substances that act as oxidizing agents, as our diagram above requires.

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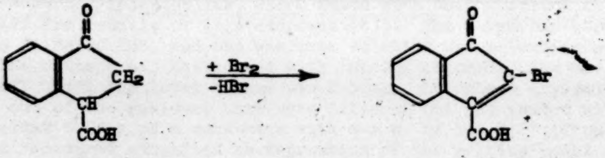
[*] After boiling 2-chloro-3-hydroxy-1,4-naphthoquinone for 48 hours in 1% sodium hydroxide with atmospheric oxygen present, for example, we secured 52% of phthalide-carboxylic, 13% of phthalic and 11% of phthalonic acids, whereas when the reaction was carried out under the same conditions, but with no atmospheric oxygen present, the yields of these acids were 14%, 2.3% and 1.2% respectively.

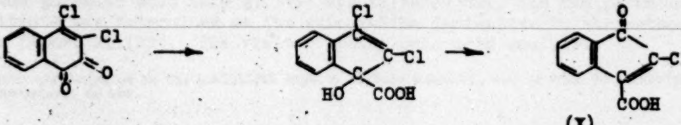
In conclusion, we must say a few words on the researches we undertook to prove the structure of indanone-1-carboxylic acid-(3) (VIII), which has not been described in the literature before this. This acid is a white substance, crystallizing from water as a monohydrate with a m.p. of 83-84° and readily giving up its molecule of crystallization water. Analysis of the acid itself and of its derivatives indicates that it has the empirical formula of $C_{10}H_8O_3 \cdot H_2O$, which also agrees with the results of determining the molecular weight of the p-nitrobenzyl ester of this acid. The titration findings and the number of active hydrogen atoms indicate that the acid molecule contains one carboxyl group. The existence of the latter was also demonstrated by the preparation of the p-nitrobenzyl ester, which crystallizes without any water of crystallization, in contrast to the acid itself. The existence of a carbonyl group in the acid molecule was proved by the preparation of the respective semicarbazone. When this acid of ours was heated in chloroform with an excess of bromine, it was readily converted into an unsaturated keto acid containing bromine, which was a yellow crystalline substance that fused with decomposition at 215-216°. The empirical formula for this acid was $C_{10}H_5O_3Br$.

Juxtaposition of the data set forth above has led us to assume that the acid that contained bromine was 2-bromoindenone-1-carboxylic acid-(3) (IX), the formation of which entailed not only the bromination of the original ketocarboxylic acid (VIII), but the evolution of hydrogen bromide as well:



(VIII) (IX)

Although 2-bromoindenone-1-carboxylic acid-(3) (IX) itself is not described in the literature, its analog containing chlorine (X) was synthesized long ago by Zincke and Englehardt [9] from 1,2-dichloro-3,4-naphthoquinone as follows:



(X)

Synthesizing 2-bromoindenone-1-carboxylic acid-(3) (IX) in the same way (from 1,2-dibromo-3,4-naphthoquinone), we secured a substance with a temp.decomp. of 215-216°, which proved to be the same as the acid containing bromine that we had recovered by brominating the acid with a m.p. of 83-84°. Lastly, chlorinating the latter compound also yielded the 2-chloroindenone-1-carboxylic acid-(3) (X), previously described by Zincke and Engelhardt [9]. It is therefore quite apparent that the substance with a m.p. of 83-84° actually is indanone-1-carboxylic acid-(3) (VIII).

EXPERIMENTAL *

1. Oxidative-Hydrolytic Transformations of 2-Pyridinium-3(1)-hydroxy-1,4(3,4)-Naphthoquinone Betaine

5.0 g of 2-pyridinium-3(1)-hydroxy-1,4(3,4)-naphthoquinone (see [10] for its preparation) was placed in 1.5 liters of a 1% aqueous solution of sodium hydroxide, and the mixture was boiled for 48 hours in a flask fitted with a reflux condenser while a gentle current of air, previously freed of its carbon dioxide, was passed through the solution. After leaving the flask, the air passed through a Tishchenko bottle filled with a 10% solution of sulfuric acid.

After the reaction was over, the pH of the solution was lowered to 7.0-7.5 by adding sulfuric acid, the solution was evaporated to a volume of some 100 ml, and, without allowing it to cool, the precipitate of silicic acid formed by the action of the alkali on the surface of the glass flask was filtered out. This precipitate was boiled three times with water, and the filtrates were combined and evaporated to a volume of about 80 ml, after which they were extracted with chloroform. Driving off the solvent yielded 1.02 g (20%) of the unreacted original quinone, with a m.p. of 290-292° (from water) [10]. The pyridine in the solution contained in the Tishchenko bottle was determined by precipitating it as the coordination compound $(CuPy_2)(CNS)_2$ with a solution of copper sulfate and a titrated solution of potassium thiocyanate. The excess of the latter was back-titrated with a solution of silver nitrate [11]. We found 0.22 g (17.5%) of pyridine.

After the extraction with chloroform, the reaction solution was acidulated with 50% sulfuric acid until its reaction was acid with Congo red, and the precipitated tarry deposit was filtered out. The latter was twice recrystallized from acetic acid containing animal charcoal. This yielded 0.45 g (15%) of 1-hydroxy-4-carboxyisoquinoline, which fused with decomposition at 295-296° (see Report XII for details of this compound [2]). The 1-hydroxy-4-carboxyisoquinoline was filtered out, and the reaction solution was re-extracted with chloroform. The extract was desiccated with calcium chloride, and the chloroform was driven off until the total volume was 2-3 ml. Colorless crystals gradually settled out of the residue; they were filtered out and washed with chloroform. This yielded 0.03 g of a substance with a m.p. of 151-152° (from water). The compound recovered exhibited no depression of the melting point when mixed with phthalidecarboxylic acid (m.p. 151-152° [12]). Yield: 1%.

After the phthalidecarboxylic acid had been leached out, the acid reaction solution was again strongly acidulated with 50% sulfuric acid and then repeatedly extracted with ether. Driving off the ether left behind a mixture of phthalic and phthalonic acids, which were separated by crystallization from water. The precipitated phthalic acid (0.9 g; 34%) was filtered out, and the phthalonic acid in the filtrate was determined as its quinoxaline derivative by the method described in Report XI [13]. The yield of phthalonic acid was 1.5%.

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* E. A. Ignatyeva participated in the analytical aspects of this research, and we wish to acknowledge our profound indebtedness to her.

When a similar test was run without allowing any atmospheric oxygen to be present, no phthalidecarboxylic or phthalonic acid was found among the reaction products (cf [2]).

2. Oxidative-Hydrolytic Transformations of 2-Benzoylamino-3-hydroxy-1,4-naphthoquinone

a) Synthesis and properties of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone. Since 2-amino-3-hydroxy-1,4-naphthoquinone is a highly unstable compound that is hard to purify and secure in the individual state [14], we used the N-benzoyl derivative of the quinone in our study of oxidative-hydrolytic transformations instead of the quinone itself. The synthesis of the 2-benzoylamino-3-hydroxy-1,4-naphthoquinone, which has not been described in the literature, and the proof of its structure are set forth below.

10.0 g of 2-nitro-3-hydroxy-1,4-naphthoquinone, produced by nitrating 3-hydroxy-1,4-naphthoquinone [14], was dissolved in 50 ml of alcohol, and 40 ml of a saturated solution of ammonia was added to the solution. This precipitated the finely crystalline yellow ammonium salt of the original quinone. Anhydrous hydrogen sulfide was passed through the water-cooled mixture for 30-45 minutes. An abundant blue precipitate gradually settled; it was filtered out, washed with alcohol, mixed with 30 ml of carbon disulfide, and allowed to stand overnight, after which it was again filtered out and washed with carbon disulfide.* It was mixed with 30 ml of a 10% solution of sodium hydroxide, and an excess of benzoyl chloride and a 10% sodium hydroxide solution were added a little at a time, with vigorous stirring, seeing to it that the solution always remained alkaline. The blue solution soon turned brownish-red, and a brown precipitate was thrown down. The substance was filtered out five hours later and washed with water. This yielded 8 g (69%) of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone. Recrystallization from glacial acetic acid containing animal charcoal yielded reddish-brown hexagonal leaflets, with a m.p. of 190.5-191°, soluble in alcohol, ether, and benzene.

Found %: C 69.81; H 4.00; N 5.10. $C_{17}H_{11}O_4N$. Computed %: C 69.62; H 3.75; N 4.77. Found (in nitrobenzene): M 291. $C_{17}H_{11}O_4N$. Computed M 293.

Number of active hydrogen atoms, determined by the Terentyev method = 1.95.

Synthesis of the azine derivative. A solution of 1.0 g of o-phenylenediamine in 10 ml of alcohol was added to 1.5 g of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone dissolved in 50 ml of alcohol, and the mixture was boiled for 2 hours. The resulting precipitate was filtered out, washed with alcohol, and recrystallized from acetic acid. This yielded a yellow crystalline substance with a m.p. of 237-239°.

Found %: C 75.38; H 3.93; N 11.50. $C_{23}H_{15}O_2N$. Computed %: C 75.61; H 4.11; N 11.29.

Splitting off benzamide. 5.0 g of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone was boiled for 70 hours in 1.5 liters of a phosphate buffer solution (pH 8.0), while a strong current of air was passed through the solution uninterruptedly. After the reaction was over, the precipitate was filtered out, and the solution was extracted with chloroform. Driving off the latter yielded 0.5 g of a substance with a m.p. of 125-127° (from water), which exhibited no depression of the melting point when mixed with benzamide. The yield was 24%.

The ability of the benzoyl derivative we had synthesized to split off benzamide under the conditions set forth above, together with the possibility of securing the respective azine from it, indicate that this derivative is an N-rather than an O-benzoyl substituted 2-amino-3-hydroxy-1,4-naphthoquinone.

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*This yielded 8.1 g (86%) of the ammonium salt of 2-amino-3-hydroxyl-4-naphthoquinone.

Behavior in a boiling solution of NaOH with atmospheric oxygen excluded. The reaction was carried out in a hydrogen atmosphere under the conditions described in Report XII [2]. We used 2.93 g of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone and 1.5 liters of a 1% solution of sodium hydroxide. The mixture was boiled for 48 hours. The brownish-red solution gradually turned purple and, after 10 hours had elapsed, cornflower blue. After the reaction was complete, 0.04 g (24%) of ammonia was found in the solution contained in the Tishchenko bottle that served as an absorbent for the gaseous reaction products. The pH of the reaction solution was lowered to 7.0 by adding sulfuric acid, and then it was evaporated in a currentof hydrogen as described in Report XII [2]. The silicic acid was filtered out, and the filtrate was acidulated with sulfuric acid. A reddish-purple precipitate of 2-amino-3-hydroxy-1,4-naphthoquinone was thrown down. Weight: 1.25 g (66%). Recrystallization from alcohol yielded it as elongated bent brown needles. It did not have a sharp melting point, changing state at about 100° [14]. Its N-benzoyl derivative fused at 190.5-191°.

After the quinone had been filtered out, the reaction solution was extracted with chloroform, and the latter was evaporated to dryness. The residue consisted of nothing but benzoic acid (weight: 0.91 g; yield: 75%). There was no phthalidecarboxylic acid.

The reaction solution left after the extraction with chloroform was extractted with ether. The ether extract was desiccated with sodium sulfate, and the ether was driven off to dryness. The residue consisted of a small amount of tarry substances. No phthalic or phthalonic acid was found.

b) Oxidative-hydrolytic cleavage of 2-benzoylamino-3-hydroxy-1,4-naphthoquinone. 2.93 g of the quinone was boiled for 48 hours with 1.5 liters of a 1% solution of sodium hydroxide under the conditions specified for Experiment 1. After the reaction was over, 0.17 g (100%) of ammonia was found in the solution used to trap the gaseous products. The pH of the reaction solution was lowered to 7.0-7.5 by adding sulfuric acid, the solution was evaporated to approximately 100 ml, the precipitated silicic acid was filtered out, and the solution was then boiled three times with water. The filtrates were combined, evaporated to 100 ml, and acidulated with 50% sulfuric acid. The traces of the original quinone were filtered out, and the solution was allowed to stand for several hours; benzoic acid (0.75 g) gradually settled out. The latter was filtered out, and the aqueous solution was extracted with chloroform. The extract was desiccated with calcium chloride, and the chloroform was driven off to small volume. As the solution cooled, white crystalline phthalidecarboxylic acid precipitated out. Weight: 0.40 g (23%). M.p. 151-152° (from water). The phthalidecarboxylic acid was filtered out, the chloroform was driven off to dryness, and the residue was recrystallized from water. This yielded 0.25 g of benzoic acid. The aggregate yield of the latter was 82%.

After the acid reaction solution had been extracted with chloroform, it was repeatedly extracted with ether. The ether was driven off, and the residual mixture of phthalic and phthalonic acids was separated by crystallization from water. The precipitated phthalic acid (0.51 g; 30%) was filtered out, and the phthalonic acid in the filtrate was determined as its quinoxaline derivative by the method described in Report XII [13]. The yield of phthalonic acid was 8%.

3. Oxidative-Hydrolytic Transformations of 2-Chloro-3-hydroxy-1,4-naphthoquinone

a) With atmospheric oxygen present. 6.3 g of 2-chloro-3-hydroxy-1,4-naphthoquinone was boiled for 48 hours with 3.75 liters of a 1% solution of sodium hydroxide under the conditions specified for Experiment 1. When the reaction was over, the solution was acidulated with hydrochloric acid until its reaction was acid with Congo red, and 2.28 g of the original quinone, with a m.p. of 214-215°, was filtered out. The pH of the filtrate was raised to 7.0-7.5 by adding alkali, the solution was evaporated to a volume of approximately 800 ml, the precipitated silicic acid was filtered out, the solution was re-evaporated to a volume of about 150 ml and re-acidulated with hydrochloric acid until its reaction was acid with Congo red, and another 0.18 g of the original quinone was filtered out. A total of 2.46 g (39%) of 2-chloro-3-hydroxy-1,4-naphthoquinone was recovered.

The acid filtrate was extracted with chloroform. Driving off the chloroform until its volume totaled 7-8 ml yielded 1.70 g (52%) of phthalidecarboxylic acid with a m.p. of 151-152° (from water). The aqueous solution left after the chloroform extraction was strongly acidulated with 50% sulfuric acid and extracted repeatedly with ether. The ether was driven off, yielding a mixture of phthalic and phthalonic acids, which were separated by crystallization from water. The precipitated phthalic acid was filtered out (weight: 0.40 g; yield: 13%), and the phthalonic acid in the filtrate was determined as its quinoxaline derivative as described in Report XI [13]. The yield of phthalonic acid was 11%.

b) With no atmospheric oxygen present. The reaction was carried out in a nitrogen atmosphere under the conditions described in Report XII [2]. 16.0 g of 2-chloro-3-hydroxy-1,4-naphhtoquinone was boiled in 8 liters of a 1% solution of sodium hydroxide for 48 hours. The reaction solution, which was dark red at first, gradually turned purple, ending up as cornflower blue after several hours had elapsed. When the reaction was over, the solution pH was lowered to 7.0-7.5 by adding sulfuric acid, and the solution was evaporated to a volume of approximately 600 ml in a nitrogen atmosphere and under the conditions specified in Report XII [2]. The precipitate thrown down was boiled several times with small amounts of acetic acid, the insoluble silicic acid being filtered out, while the acetic acid filtrates were combined and evaporated to small volume. When the concentrated solution cooled, 2.1 g of isonaphthazarine settled out. After the precipitate had been filtered out, the reaction solution was acidulated with sulfuric acid, yielding another 6.1 g of isonaphthazarine, with a m.p. of 281-282° (from acetic acid). The aggregate yield was 56%.

The isonaphthazarine was filtered out, and the reaction solution was extracted with chloroform. The extract was desiccated with calcium chloride, and the chloroform was driven off to a volume of 15-20 ml. As it cooled, 1.9 g (14%) of phthalidecarboxylic acid, with a m.p. of 151-152° (from water), gradually settled out. After the phthalidecarboxylic acid had been filtered out, the chloroform solution was evaporated to dryness. The residue consisted of 2.9 g of a dark, noncrystallizing oil. 60 ml of water was added to the oil, and the mixture was heated to boiling, causing nearly all of the substance to dissolve. An excess of an aqueous solution of lead acetate was added to the hot solution to remove any traces of isonaphthazarine, and the blue lead salt of isonaphthazarine that settled was filtered out. The excess lead ions were precipitated with sulfuric acid, and the solution was filtered, boiled with animal charcoal, and extracted with chloroform. The chloroform was driven off, yielding 2.7 g (18%) of indanone-1-carboxylic acid-(3) with a m.p. of 83-84° (from water). After the aqueous reaction solution had been extracted with chloroform, it was repeatedly extracted with ether. The ether extract was desiccated with sodium sulfate, and the ether was driven off. The dry residue was triturated twice with 15-20 ml of chloroform, filtered out, and crystallized from a small amount of water in order to remove any traces of phthalidecarboxylic acid or impurities. This yielded 0.3 g (2.3%) of phthalic acid, the phthalonic acid in the mother liquor being determined as its quinoxaline derivative by the method specified in Report XI [13]. The yield of phthalonic acid was 1.2%.

4. Properties and Transformations of Indanone-1-Carboxylic Acid-(3)

The substance crystallized from water as its monohydrate (elongated colorless leaflets with a m.p. of 83-84°). It was readily soluble in chloroform, ether, and benzene. When these solvents were driven off, it remained in the form of an oil, crystallizing only when water was added.

Found %: C 61.86; H 5.15. $C_{10}H_{10}O_4$. Computed %: C 61.85; H 5.15.

Determination of water. The air-dry substance was desiccated to constant weight above calcium chloride in a vacuum desiccator.

Found %: H_2O 8.85; $C_{10}H_8O_3 \cdot H_2O$. Computed %: H_2O 9.26. Titration data (in 10% alcohol with phenolphthalein). Found: M 197. $C_8H_7O(COOH) \cdot H_2O$. Computed: M 194.

Number of active hydrogen atoms, by the Terentyev method (in pyridine) = = 3.18.

Semicarbazone. 1.0 g of the substance was dissolved in 10 ml of alcohol, and 0.5 g of semicarbazide hydrochloride and 0.5 g of potassium acetate dissolved in 5 ml of water were added to the resulting solution. The crystalline semicarbazone gradually precipitated out; it was filtered out and recrystallized from alcohol. Temp. decomp. 213°.

Found %: N 17.81. $C_{11}H_{11}O_3N_2$. Computed %: N 18.02.

p-Nitrobenzyl ester. 0.5 g of the substance was neutralized with a calculated quantity of a 0.1 N solution of sodium hydroxide. To the resulting solution we added twice the volume of alcohol and 0.7 g of p-nitrobenzyl bromide. The mixture was boiled for 1 hour, and the precipitate that settled when it cooled was filtered out. This yielded 0.32 g (40%) of the ester, with a m.p. of 110-111° (from alcohol).

Found %: C 65.31; H 4.04. $C_{17}H_{13}O_5N$. Computed %: C 65.59; H 4.17.
The molecular weight was determined cryoscopically in nitrobenzene.
Found: M 313, 310. $C_{17}H_{13}O_5N$. Computed: M 311.

Bromination of indanone-1-carboxylic acid-(3). 1.0 g of the substance was dissolved in 15 ml of chloroform, and a solution of bromine in chloroform was gradually added to the boiling solution until no more bromine was absorbed. After the chloroform was driven off, the residue was washed twice with small quantities of hot water and recrystallized from acetic acid, benzene, or chloroform. This yielded 0.3 g (23%) of 2-bromindenone-1-carboxylic acid-(3). Yellow leaflets; m.p. 215-216° (with decomp.).

Found %: C 47.23; H 2.18; Br 31.49. $C_{10}H_5O_3Br$. Computed %: C 47.44; H 1.97; Br 31.60

The synthesized substance exhibited no depression of the melting point when mixed with the 2-bromoindenone-1-carboxylic acid-(3) we had synthesized by the method described earlier [9] for 2-chloroindenone-1-carboxylic acid-(3).

Synthesis of 2-bromoindenone-1-carboxylic acid-(3). 10 g of 1,2-dibromo-3,4-naphthoquinone was triturated with a small quantity of water, and then 60 ml of a 10% solution of sodium hydroxide was added. The quinone dissolved quickly, turning the solution dark brown. Hydrochloric acid was added to the solution until its reaction was slightly acid, and the precipitated tarry deposit was filtered out. The filtrete was shaken for 5-10 minutes with animal charcoal, filtered, and acidulated with strong hydrochloric acid. A heavy brown oil settled out, which was separated from the aqueous layer and dissolved in 25 ml of glacial acetic acid; 25 ml of concentrated sulfuric acid was added and then the resultant solution was heated for one hour over a water bath. As the solution cooled, a red substance settled out. The mixture was poured into water, and the precipitate was filtered out, washed with water, and recrystallized from acetic acid or benzene. This yielded 6.5 g (81%) of 2-bromoindenone-1-carboxylic acid-(3), with a m.p. of 215-216° (with decomp.).

Chlorination of indanone-1-carboxylic acid-(3). 1.0 g of the substance was dissolved by heating it in 15-20 ml of chloroform, and a current of chlorine was passed through the boiling solution for 30 minutes. The chloroform was driven off, and the residue was washed three times with hot water and recrystallized from glacial acetic acid or benzene. This yielded 0.2 g (18%) of a substance with a m.p. of 223-224° (with decomp.), which melted at the same temperature when mixed with the 2-chloroindenone-1-carboxylic acid-(3) synthesized from 1,2-dichloro-3,4-naphthoquinone [[illegible]].

SUMMARY

It has been found that substituted 3-hydroxy-1,4-naphthoquinones that contain a hydroxyl group, a chlorine atom, an amino group, or a pyridinium radical at the 2 position undergo monotypic transformations in the presence of oxidizing and hydrolyzing agents, resulting in the cleavage of the quinone ring in all of these compounds, together with the splitting off of the substituents at the 2 position. In every case the terminal compounds are phthalic, phthalonic, and phthalidecarboxylic acids. It has been shown that reactions of this sort involve an intermediate stage in which 1,2,3,4-tetraoxotetralin is formed, which is then converted into the terminal acids specified.

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USING KETENE AS AN ACETYLATING AGENT

II. SOME NEW FINDINGS ON THE ACETYLATION OF ALCOHOLS

A. A. Ponomarev and Yu. B. Isayev

The action of ketene upon aliphatic alcohols is one of the most thoroughly investigated reactions of the former.

The reaction rate has been studied as a function of the chemical nature and the structure of the alcohol [1,2,3], and the effect of various catalytic additives and other reaction conditions has been investigated.

Several substances of different chemical character and effectiveness have been proposed for the acetylation of the lower aliphatic alcohols, such as: sulfuric acid, sulfo acids, sodium acetate, sulfuric acid amide, etc. Morey, in particular, noted [3] that sodium acetate was less active than sulfuric acid in acetylating the aliphatic alcohol n-butanol. We have found, however, that sodium acetate is a good catalyst for the acetylation of glycols [4].

Some authors recommend acetylating without catalysts, at the boiling points of the alcohols to be acetylated [2].

Notwithstanding all the research that has been done on the reactions of ketene with alcohols, the data on the yields of the corresponding esters are often contradictory [5,2] or are lacking altogether. Of the higher aliphatic alcohols, research has been done on cetyl alcohol [2], geraniol [6], and linalool [6,7].

According to Tsukervanik and Yermolenko, linalool, for example, yields an ester with a yield of 49% of the theoretical when reacted with ketene without a catalyst, whereas Nametkin and Fedoseev managed to secure a yield that was only 2.3-4.2% of the theoretical, though they employed a more than sevenfold excess of ketene.

We acetylated a primary heptyl and a secondary octyl alcohol without a catalyst and with the addition of potassium bisulfate as a catalyst. We have already reported on the use of $KHSO_4$ in the acetylation of monoethylamine, it proving to be less effective than sodium acetate. Using $KHSO_4$ with the abovementioned alcohols, however, makes it possible to achieve yields of 80% of the respective esters.

This led us to test potassium bisulfate with the lower alcohols - propyl and n-butyl alcohols and fusel oil; the acetate yields were also high.

We also tested potassium bisulfate as a catalyst for acetylating furyl alcohol, the literature containing no information on its acetylation with ketene. Potassium bisulfate proved to be ineffective in the production of furyl acetate, probably because of the acidophobic property of the furan ring. Sulfuric acid is useless in acetylating furyl alcohol for the same reason. We did manage to secure positive results, however, by employing urea as a catalyst for acetylating furyl alcohol, the yield of furyl acetate being 76.5% of the theoretical. We found that mixtures of urea and $KHSO_4$ in various proportions also exhibited the tarring action of the bisulfate when used with furyl alcohol.

EXPERIMENTAL*

The ketene was prepared by the pyrolysis of acetone in an apparatus of our own design, providing recycling of the acetone.

Acetylation was effected by bubbling the ketene through the substance to be acetylated in the reactor; a thermometer was immersed in the liquid. The end of the reaction was indicated by the temperature of the reaction mixture dropping to its initial value. The ester numbers of the reaction products were determined by the usual method: with an alcoholic solution of KOH, followed by back-titrating the latter with 0.5 N H_2SO_4, in the presence of phenolphthalein.

I. Acetylation of Primary Heptyl Alcohol

Heptyl alcohol: b.p. 175-178°; $n_D^{26.5}$ 1.4220.

Test 1. For this reaction we used 6 g of the heptyl alcohol without any additive. The reaction mixture reached its maximum temperature (62°) in 30 minutes. The reaction mixture was transparent and slightly yellow. The results of fractionating the reaction products at atmospheric pressure are tabulated in Table 1.

TABLE 1

Fraction No.	Boiling point, °	Weight, grams	n_D^{31}	Ester No., experimental	Ester No. of heptyl acetate calculated	Per cent of heptyl acetate
1	75-100	0.46	–	–	–	–
2	177-185	0.31	1.4112	–	–	–
3	185-190	5.71	1.4110	330.40 333.30	354.00	93.45

Analysis of the 185-190° fraction:
0.0990 g substance: 0.2474 g CO_2; 0.1018 g H_2O. Found %: C 68.20; H 11.51. $C_9H_{18}O_2$. Computed %: C 68.51; H 11.41. $C_7H_{16}O$. Computed %: C 72.35; H 13.88.

The yield of the acetate of the primary heptyl alcohol was 65.5% of the theoretical.

Test 2. We acetylated 7.90 g of the heptyl alcohol with 0.2 g of potassium bisulfate. The reaction mass remained transparent, but acquired a barely perceptible yellowish tinge. Gain in weight: 5.10 g.

The results of fractionating the reaction products at atmospheric pressure are tabulated in Table 2.

Analysis of the 185-192° fraction:
0.1001 g substance: 0.2501 g CO_2; 0.1035 g H_2O. Found %: C 68.41; H 11.52. $C_9H_{18}O_2$. Computed %: C 68.51; H 11.41.

The yield of the acetate of the primary heptyl alcohol was 80% of the theoretical.

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*V. L. Lipovskaya assisted in the experimental section of this research.

TABLE 2

Fraction No.	Boiling point, °	Weight, grams	n_D^{17}	Ester No., experimental	Ester No., calculated	Per cent of heptyl ester
1	To 100	0.96	1.3655	-	-	-
2	To 177	0.36	1.3981	-	-	-
3	177-185	0.80	1.4143	319.42	-	90.23
4	185-192	8.28	1.4162	349.30	354	98.67
	Residue	0.96				

II. Acetylation of Secondary Octyl Alcohol

Octyl alcohol: b.p. 177-179°; $n_D^{26.5}$ 1.4220.

Test 1. We acetylated 6 g of the octyl alcohol without any additive. The reaction mixture reached its maximum temperature (54°) after 35 minutes. The reaction mixture was transparent and slightly yellow. The results of fractionating the reaction products at atmospheric pressure are tabulated in Table 3.

TABLE 3

Fraction No.	Boiling point, °	Weight, grams	$n_D^{26.3}$	Ester No., experimental	Ester No. of octyl acetate, calculated	Per cent of octyl acetate
1	To 100	0.40	-	-	-	-
2	120-125	0.19	1.3900	-	-	-
3	187-193	4.74	1.4129	243.70 244.80	325.00	75.08

Test 2. We acetylated 7.78 g of the octyl alcohol with 0.2 g of potassium bisulfate. The reaction mixture remained transparent, but acquired a barely perceptible yellowish tinge. Gain in weight: 4.67 g. The results of fractionating the reaction products at atmospheric pressure are tabulated in Table 4.

TABLE 4

Fraction No.	Boiling point, °	Weight, grams	n_D^{17}	Ester No., experimental	Ester No., calculated	Per cent of octyl acetate
1	To 100	1.88	-	-	-	-
2	To 187	2.05	1.4077	188.90	-	58.12
3	187-193	7.20	1.4166	314.06	325	96.63
	Residue	0.72	-	-	-	-

Analysis of the 187-193° fraction:
0.0955 g substance: 0.2439 g CO_2; 0.10047 g H_2O. Found %: C 70.11; H 11.81.
$C_{10}H_{20}O_2$. Computed %: C 70.13; H 11.74.

The yield of the acetate of the secondary octyl alcohol was 80% of the theoretical.

III. Acetylation of n-Propyl Alcohol

Propyl alcohol: b.p. 96-98°; n_D^{24} 1.3833.

The catalyst – potassium bisulfate – was prepared as follows to ensure better distribution throughout the alcohol: 0.2 g of potassium bisulfate and 0.2 g of water were placed in the reactor. After a supersaturated solution of $KHSO_4$ had been produced in the reactor, 16.18 g of the propyl alcohol was added; the mixture was stirred, so that the potassium bisulfate was distributed throughout the alcohol as a fine suspension. The reactor was chilled with cold water during the ketene acetylation; vapor traps, which also contained potassium bisulfate, were attached to the reactor to diminish the loss due to entrainment of the alcohol by the current of gas. When the reactor's gain in weight exceeded the theoretical amount somewhat, the reaction was considered complete. After the bisulfate had been neutralized (with chalk or soda), the propyl acetate was distilled at 99-104°. The yield of acetate with n_D^{25} 1.38178 was 24.51 g, equivalent to 87% of the theoretical.

IV. Acetylation of n-Butyl Alcohol

The butyl alcohol (b.p. 115-117°) was acetylated under the same conditions. The alcohol weighed 10.16 g. The product was fractionated after the bisulfate had been neutralized and the acetone had been driven off. The yield of butyl acetate (b.p. 124-127° and n_D^{24} 1.3921) was 13.82 g, or 87% of the theoretical.

The same conditions were employed to acetylate 60 g of fusel oil, desiccated with copper sulfate, the acetylation being 72% effective according to preliminary data.

V. Acetylation of Furyl Alcohol

In these tests we employed furyl alcohol with a b.p. of 80° (15 mm); n_D^{22} 1.4889.

Test 1. We acetylated 6.07 g of furyl alcohol without any additive. Gain in weight: 4.10 g. The results of fractionating the 7.79 g of reaction product in a 15-mm vacuum are tabulated in Table 5.

TABLE 5

Fraction No.	Boiling point, °	Weight, grams	n_D^{18}	Ester No., experimental	Ester No. of furyl acetate, calculated	Per cent of furyl acetate
1	To 78	0.28	1.4617	–	–	–
2	78-85	4.50	1.4679	341.56	400.53	85.26
3	85-87.5	1.22	1.4668	355.01		88.62
	Residue	1.39	–	–	–	–

The yield of furyl acetate was 56.5% of the theoretical.

Test 2. We acetylated 15.08 g of furyl alcohol with 0.15 g of potassium bisulfate. The gain in weight was 11.32 g. After neutralization and the driving off of the acetone the reaction product was fractionated at 15 mm. The 67-82° fractions were collected (totalling 21.45 g). A brownish-red tarry residue totalling 5.40 g was left in the distilling flask, evidence of the tarring action of potassium bisulfate.

Test 3. 15.15 g of furyl alcohol with the addition of one-half of one per cent of urea was acetylated with ketene. The gain in weight was 10.22 g. After the acetone had been driven off, the 21.53 g of the reaction product (n_D^{22} 1.4511) was fractionated at 15 mm. The fractionation results are tabulated in Table 6.

TABLE 6

Fraction No.	Boiling point at 15 mm, °	Weight, grams	n_D^{22}	Ester No., experimental	Ester No. of furyl acetate, calculated	Per cent of furyl acetate
1	To 67	2.73	1.4151	-	-	-
2	67-76	0.21	1.4433	-	-	-
3	76-80.5	17.14	1.4629	386.44 388.80	400.58	96.76
	Residue	0.95	-	-	-	-

Analysis of the 76-80.5° (15 mm) fraction:
0.1260 g substance: 0.2760 g CO_2; 0.0676 g H_2O. Found %: C 59.78; H 6.00. $C_7H_8O_3$. Computed %: C 59.99; H 5.76. $C_5H_6O_2$. Computed %: C 61.21; H 6.17.

The yield of furyl acetate was 76.5% of the theoretical.

Test 4. 15.08 g of furyl acetate was acetylated with a mixture of 0.15 g of potassium bisulfate and 0.15 g of urea. The gain in weight was 8.77 g. The product was fractionated at 15 mm after neutralization and after the acetone had been driven off. We collected the fractions that distilled at 67-85° (totalling 12.97 g). A brownish-red residue totaling 6.07 g was left in the distilling flask, evidence of the tarring action of potassium bisulfate upon furyl alcohol during the process of acetylation.

SUMMARY

1. A primary heptyl and a secondary octyl alcohol have been acetylated with ketene in the presence of potassium bisulfate. It has been found that with this catalyst the yields of the acetates of these alcohols are 80% of the theoretical; the ester yields are 65.5 and 45%, respectively, when no catalyst is used.

2. It has been found that the lower aliphatic alcohols (propyl and butyl alcohols) are acetylated with high yields (as much as 87%) by ketene when small amounts of a solution of potassium bisulfate in water are added.

3. Furyl alcohol has been acetylated with ketene. It has been found that adding a small amount of urea makes it possible to raise the yield of furyl acetate to 76.5% of the theoretical.

4. Acid additives ($KHSO_4$, H_2SO_4) cannot be used in the acetylation of furyl alcohol as they produce considerable tarring.

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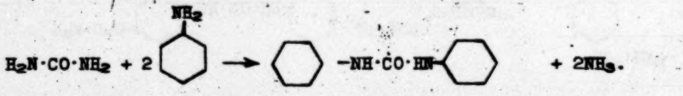
*See CB translation p. 1121 ff.

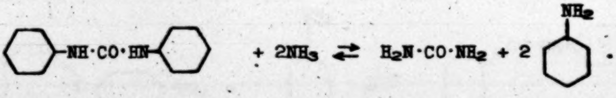
THE REACTION OF DINITRODIPHENYLUREA WITH AROMATIC AMINES

I. M. Kogan and D. F. Kutepov

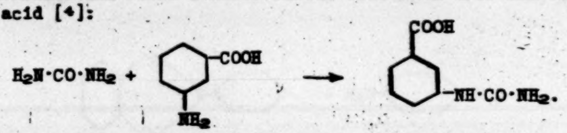
Much research has been done on the reaction of urea with aromatic amines. As far back as 1864, for example, carbanilide was synthesized by heating 1 part of urea with 3 parts of aniline to 150-170° [1].


NH₂
H₂N·CO·NH₂ + 2
–NH·CO·HN
+ 2NH₃.

Monophenylurea could also be synthesized under these conditions by reducing the amount of aniline used [2]. This is a reversible reaction, since aniline and urea can be secured by heating carbanilide to 150° in a sealed tube with an alcoholic solution of ammonia [3]:

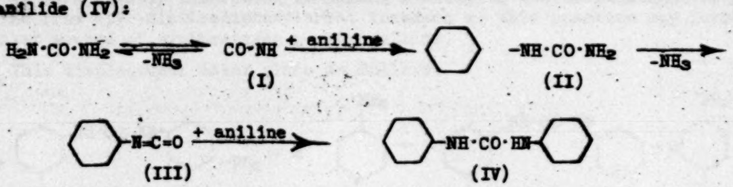

NH·CO·HN
+ 2NH₃
H₂N·CO·NH₂ + 2
NH₂

N.A.Menshutkin fused m-aminobenzoic acid with urea and secured m-carbamidobenzoic acid [4]:


H₂N·CO·NH₂ +
COOH
NH₂
COOH
NH·CO·NH₂.

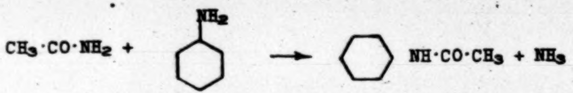
The process for securing carbanilide by the action of aniline upon urea is considerably improved by adding an acid as a catalyst [5].

In his study of analogous reactions, Davis [6] concluded that urea dissociates when it is heated to 160°, evolving ammonia and isocyanic acid (I); the latter reacts with aniline, forming phenylurea (II). At the reaction temperature (160°), the phenylurea splits off ammonia and is converted into phenyl isocyanate (III). As we know, phenylisocyanate reacts readily with aniline to form carbanilide (IV):

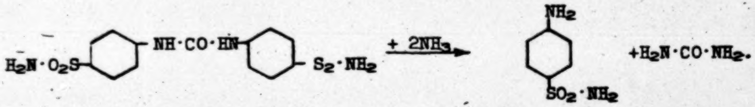

H₂N·CO·NH₂
-NH₃
CO–NH
(I)
+ aniline
–NH·CO·NH₂
(II)
-NH₃
N=C=O
(III)
+ aniline
NH·CO·HN
(IV)

Alkyl derivatives of urea can enter into transformations of this sort as readily as urea itself. When symmetrical diethylurea is reacted with two molecules of aniline, for instance, carbanilide and two molecules of ethylamine are formed [6].

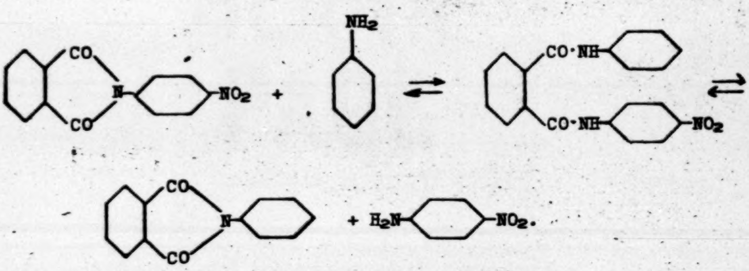
The monoamides of fatty acids react in the same way, as has been shown by P.I.Petrenko-Kritchenko and R.P.Kaplun in the reaction of acetamide with aniline [7]:



The paper by G.I.Braz, M.V.Lizgunova, and A.A.Chemerisskaya [8], and that of M.P.Gerchuk [9], in which the authors found that heating diphenylurea disulfamide with ammonia yielded sulfanilimide and urea, are also of interest.



There is an exceptionally large number of researches on the reaction of amines with the amides of phthalic acid. Lesser [10] pointed out that p-nitroaniline is evolved when N-4'-nitrophenylphthalimide was heated with aniline in an autoclave to 170-180° for 0.5-1 hour.

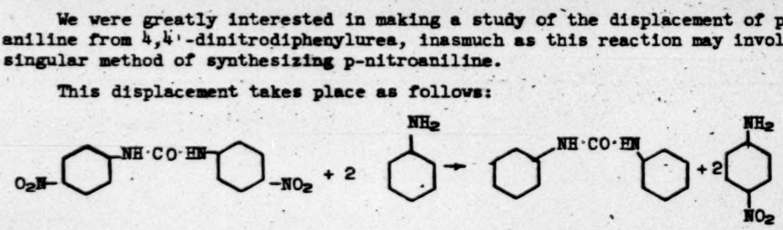


B.A.Porai-Koshits [11] proved the reversibility of reactions of this type, using as examples this kind of transformations.

The transformations described above may be regarded as a reaction involving the acylation of aromatic amines by amides of carboxylic acids or as a reaction involving the "displacement" of an amine by an aromatic amine, yielding an amide.

We were greatly interested in making a study of the displacement of p-nitroaniline from 4,4'-dinitrodiphenylurea, inasmuch as this reaction may involve a singular method of synthesizing p-nitroaniline.

This displacement takes place as follows:



4,4'-Dinitrodiphenylurea (4,4'-dinitrocarbanilide) is mixed with aniline, and the mixture is heated with a reflux condenser to 150-180° above an oil bath. The dinitrocarbanilide dissolves in the aniline, forming a homogenous solution. When the process is complete, the reaction mass solidifies in the flask.

In order to get the mass out of the flask, 10% hydrochloric acid is added, and the mixture is heated to 100°. (As we had found earlier, neither carbanilide nor 4,4'-dinitrocarbanilide is hydrolyzed under these conditons.) This treatment dissolves the excess aniline and the p-nitroaniline, the deposit containing the carbanilide, whose m.p. varies between 208 and 230.5°. Recrystallization from glacial acetic acid yields the chemically pure carbanilide with a m.p. of 239°. The solution, containing the hydrochlorides of aniline and of p-nitroaniline, is alkalinized, and then the aniline is driven off with steam. The precipitate of p-nitroaniline is filtered out. Recrystallization yields chemically pure p-nitroaniline with a m.p. of 147°.

At the start the reagent proportions were 1 mole of 4,4'-dinitrocarbanilide to 2 moles of aniline plus a slight excess of some 8%. This produced a p-nitroaniline yield that was 67.18% of the theoretical. Increasing the amount of aniline to 3.2 moles per mole of 4,4'-dinitrocarbanilide, with a temperature of 180° and a reaction time of 30 minutes, raised the yield of p-nitroaniline considerably, to 97.08% of the theoretical. We were later able to shorten the reaction time still further (all other conditions remaining the same) to 15 minutes, the yield of p-nitroaniline attaining 99.12%.

Our study of the effect of the process time upon the yield of p-nitroaniline resulted in the curve reproduced in Fig. 1. As we see from the figure, the optimum process time is 15 minutes. The yield of p-nitroaniline drops off slowly as the time is prolonged, the yield falling to 84.8% when the process is run for 5 hours; the drop in yield is paralleled by a considerable amount of tarring.

Temperature has an even more pronounced effect upon the displacement reaction (Fig. 2). The maximum yield of p-nitroaniline, 99.1%, is secured at 180° (with a process time of 15 minutes).

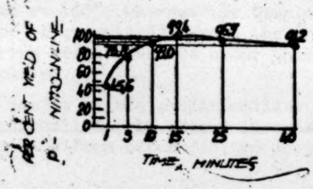


Fig. 1. Effect of the process time upon the 'displacement' of p-nitroaniline by aniline from p,p'-dinitrocarbanilide.

The p-nitroaniline yield drops off sharply at higher or lower temperatures.

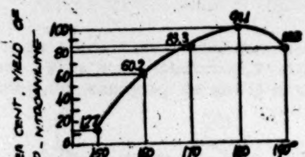


Fig. 2. Effect of temperature upon the displacement of p-nitroaniline by aniline from p,p'-dinitrocarbanilide.

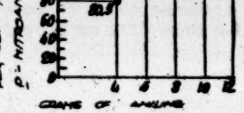


Fig. 3. Effect of the amount of aniline upon the displacement of p-nitroaniline by aniline from p,p'-dinitrocarbanilide.

The proportion of aniline used in this reaction does not exert so marked an effect. The best proportions were found to be 3.2 moles of aniline per mole of 4,4'-dinitrocarbanilide (1 part of aniline to 1 part of dinitrocarbanilide). Any further increase in the amount of aniline causes the p-nitroaniline yield to fall, so that using 6.4 moles of aniline per mole of 4,4'-dinitrocarbanilide yields only 86.7% of p-nitroaniline (Fig. 3).

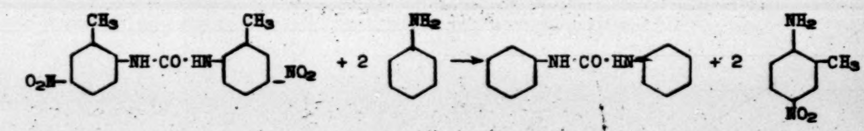
The reaction mass is fairly mobile when it is heated, but it becomes highly viscous toward the end of the reaction, which may be the cause of a certain amount of tarring. It was therefore of some interest to try the displacement process in some neutral organic solvent. We used ethylene glycol as this solvent since it had a high boiling point and was a fairly good solvent of both the 4,4'-dinitrocarbanilide and the anilide.

Here we observed an interesting phenomenon, namely, the yield of p-nitroaniline always remained unchanged, no matter how much ethylene glycol was used, all other conditions remaining the same. For example, when we used 3 g of ethylene glycol, the yield of p-nitroaniline was 5.1 g; the yield of p-nitroaniline was 5.1 g with 10 g of ethylene glycol; and, lastly, the yield of p-nitroaniline was 5.1 g with 6 g of ethylene glycol. Moreover, the melting point of the resultant p-nitroaniline was practically identical in every case. When the temperature was raised to 190-195° and 6 g of ethylene glycol was used, the yield of p-nitroaniline rose to 99.80%.

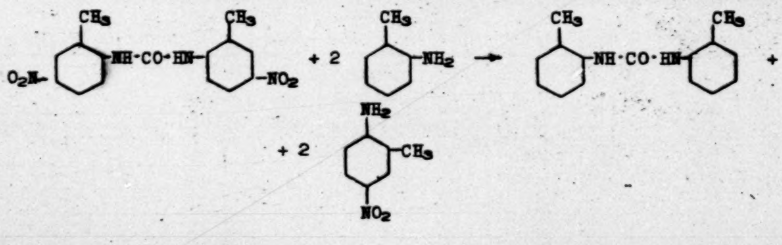
We may conclude from these observations that the amount of ethylene glycol has no effect upon the yield of p-nitroaniline at 180°, whereas the displacement of p-nitroaniline from 4,4'-dinitrocarbanilide is quantitative when the temperature is raised to 190-195°, considerable tarring being observed under these latter conditions when no ethylene glycol is employed.

In view of the high yields and the high purity of the p-nitroaniline secured by displacement by aniline from 4,4'-dinitrocarbanilide, it seemed interesting to test the feasibility of displacing nitroaniline from other dinitro derivatives of carbanilide.

Our work has shown that heating 3,3'-dinitrocarbanilide with aniline to 180° for 15 minutes yields about 80% of m-nitroaniline; furthermore, when 4,4'-dinitro-2,2'-dimethylcarbanilide is heated to 180° with aniline for 1 hour, we get 3-nitro-2-toluidine:



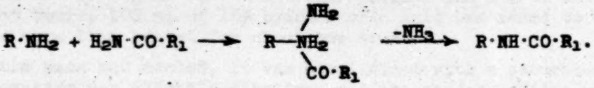
In these transformations the aniline may be replaced by other aromatic amines. When 4,4'-dinitro-2,2'-dimethylcarbanilide is heated to 201° with o-toluidine, for example, we get 3-nitro-2-toluidine:



Since B.A.Porai-Koshits [11] found that the displacement reaction is a reversible one, we tried to investigate the reversibility of the reaction involving the displacement of p-nitroaniline by aniline from 4,4'-dinitrocarbanilide. As we know, M.P.Gerchuk and his co-workers [13] assert that this reaction does not occur. We placed 5 g of the carbanilide and 25 g of p-nitroaniline in a reaction flask. The reaction mass was heated to 170° for an hour. The aniline formed in the reaction was steam distilled, extracted with ether, diazotized, and back-titrated with nitrite. The consumption of nitrite indicated that 1.6 g of aniline had been displaced as a result of the reaction, or 37% of the theoretical, based on the carbanilide. Separating and purifying the residue left in the flask after the aniline had been driven off yielded 2.15 g of 4,4'-dinitrocarbanilide with a m.p. of 310.5°.

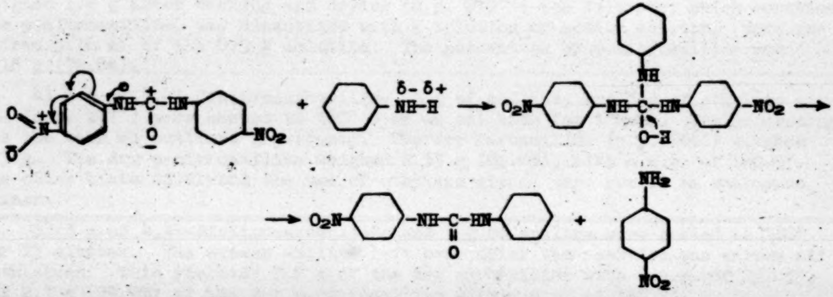
This reaction requires a considerable excess of p-nitroaniline, in contrast to the reverse reaction involving the displacement of the p-nitroaniline by aniline.

The first explanation of the mechanism of a displacement reaction was suggested by B.A.Porai-Koshits [11]; he believed that this process involved a stage in which the amide was added to the amine as follows:



$$R\cdot NH_2 + H_2N\cdot CO\cdot R_1 \longrightarrow R-\overset{NH_2}{\underset{CO\cdot R_1}{NH_2}} \xrightarrow{-NH_3} R\cdot NH\cdot CO\cdot R_1.$$

In our opinion the addition of the aniline to the tautomeric form of the dinitrocarbanilide or, more precisely, to the previously polarized molecule of dinitrocarbanilide was more likely:



The secondary polarization of the molecule leads to addition of another molecule of aniline, and so forth. The presence of the nitro group, which attracts electrons, facilitates the polarization of the keto group, and, hence, promotes the displacement process. When no nitro group is present, it is harder for polarization of the molecule to set in, whence it follows that the displacement of aniline by p-nitroaniline must be harder, resulting in lower yields of aniline. This is borne out, as we have seen in practice.

EXPERIMENTAL

Displacement of p-Nitroaniline by Aniline

1) A mixture of 3 g (1 mole) of recrystallized 4,4'-dinitrocarbanilide, prepared by phosgenizing p-nitroaniline [2], with a m.p. of 310°, and 2 g (2 moles) of aniline was boiled with a reflux condenser at 180° for 1 hour.

After the mixture had cooled, 100 ml of 10% hydrochloric acid was added, and the whole was boiled for 1 hour, being filtered after it had cooled. The precipitated carbanilide was washed with cold 10% hydrochloric acid and with water and dried. The yield of dry carbanilide was 1.52 g with a m.p. of 212° (unpurified), the m.p. being 239° after recrystallization from glacial acetic acid. The filtrate was alkalinized with soda, and the precipitated p-nitroaniline was washed on the filter and dried, it weighed 1.83 g (67.18% of the theoretical); its m.p. was 146°, rising to 147° after a single recrystallization from water. A sample fused at 147° when mixed with chemically pure p-nitroaniline.

4.975 mg substance: 12.882 mg CO_2; 2.620 mg H_2O. 2.980 mg substance: 7.994 mg CO_2; 1.586 mg H_2O. Found %: C 73.28, 73.16; H 6.12, 5.96. $C_{13}H_{12}ON_2$. Computed %: C 73.58; H 5.66.

2) A mixture of 3 g of 4,4'-dinitrocarbanilide and 3 g of aniline was heated to 180° for 30 minutes. This yielded 2.66 g of the dry aniline with a m.p. of 143.5° (m.p. 147° after a single recrystallization from water). The yield of the commercial product was 97.08%.

3) A mixture of 3 g of 4,4'-dinitrocarbanilide and 3 g of aniline was heated to 180° for 3 hours; 100 ml of 10% hydrochloric acid was added to the flask, and the contents were then heated for about one hour.

After the mass had cooled, it was alkalinized with a saturated soda solution until its reaction was slightly alkaline, and the excess aniline was driven off with steam until the distillate no longer exhibited the characteristic color with bleaching powder. After the aniline had been driven off, the mass was reacidified with hydrochloric acid and heated to 40°. The precipitated carbanilide weighed 1.8 g after washing and drying (m.p. 210°); the filtrate, which contained the p-nitroaniline, was diazotized with a solution of sodium nitrite. This required 3.16 ml of the 0.5 N solution. The percentage of p-nitroaniline was 2.18 g (79.6%).

4) 3 g of 4,4'-dinitrocarbanilide, 3 g of aniline, and 8 g of ethylene glycol (b.p. 197°) were heated to 180° over an oil bath for 1 hour. The processing was the same as outlined previously. The dry carbanilide (m.p. 206°) weighed 0.3 g. The dry p-nitroaniline weighed 2.33 g (85.0%), with a m.p. of 140.5°. The other tests involving the use of ethylene glycol were run in an analogous manner.

5) 3 g of 4,4'-dinitrocarbanilide and 3 g of aniline were heated to 180° for 15 minutes. The excess aniline left over after the reaction was driven off with steam. This yielded: 3.2 g of the dry carbanilide with a m.p. of 221.5°, and 2.7 g (99.2%) of the dry p-nitroaniline with a m.p. of 146.5°.

6) 6 g (1 mole) of m,m'-dinitrocarbanilide, with a m.p. of 240°, prepared by phosgenizing m-nitroaniline, was heated to 180° with 6 g (3 moles) of aniline for 15 minutes. The processing was the same as above. This yielded 4.08 g (74.5%) of m-nitroaniline with a m.p. of 114°. A sample of this product exhibited no depression when fused with chemically pure m-nitroaniline.

7) 5 g (1 mole) of 4,4'-dinitro-2,2'-dimethylcarbanilide, with a m.p. of 300°, prepared by phosgenizing p-nitro-o-toluidine, and 5 g (3 moles) of aniline were heated to 180° for one hour. The processing was the same as that described above. Alkalinization of the filtrate yielded 3.29 g of commercial p-nitro-o-toluidine, with a m.p. of 104.5°. Double recrystallization from water raised the melting point to 126°; the yield of refined p-nitro-o-toluidine was 2.1 g.

8) 2.5 g of 4,4'-dinitro-2,2'-dimethylcarbanilide and 2.5 g of o-toluidine were heated to 201° for one hour. The mass was processed with 10% of hydrochloric

acid, as before. The precipitated 2,2'-dimethylcarbanilide fused at 235° after recrystallization from glacial acetic acid. Alkalinization of the filtrate yielded 1.3 g of the dry yellow precipitate of p-nitro-o-toluidine, m.p. 105°. Triple recrystallization from water yielded 0.9 g of p-nitro-o-toluidine with a m.p. of 126.5°.

9) 5 g (1 mole) of carbanilide and 25 g (about 8 moles) of p-nitroaniline were heated to 170° for about 1 hour. The resultant aniline was driven off with steam. The amount of 0.5 N sodium nitrite solution consumed indicated that aniline amounted to 1.6 g (37%, based on the carbanilide). The residue left in the flask (after the aniline had been driven off) weighed 3.8 g after separation and drying; m.p. 297°. This product was treated with ethyl alcohol, yielding a precipitate with a m.p. of 303° (after drying) and an alcoholic filtrate; dilution of the filtrate with water yielded a light-pink precipitate of carbanilide with a m.p. of 239.5°. Recrystallization of the precipitate with a m.p. of 303° from glacial acetic acid yielded 2.15 g of 4,4'-dinitrocarbanilide, with a m.p. of 310.5° (Yield: 30.2%). A mixture of the latter product with chemically pure 4,4'-dinitrocarbanilide fused at 310-311°.

Analysis: 3.690 mg substance: 0.945 mg CO_2; 1.180 mg H_2O. 2.036 mg; 0.334 mg N_2 (20°, 731 mm). $C_{13}H_{10}O_5N_4$. Computed %: C 51.65; H 3.31; N 18.54. Found %: C 51.34; H 3.58; N 18.40.

SUMMARY

1. When 4,4'-dinitrocarbanilide is reacted with aniline, p-nitroaniline is "displaced" by the aniline and carbanilide is formed.

2. The "displacement" reaction is nearly quantitative after 15 minutes at the boiling point of aniline.

3. The "displacement" reaction is a reversible reaction; the reverse process of "displacing" aniline from carbanilide by p-nitroaniline requires a large excess of p-nitroaniline.

4. The "displacement" reaction may be employed by other dinitro derivatives of carbanilide in addition to the 4,4'-dinitrocarbanilide.

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AZO DYES FROM 1,5-AMINONAPHTHOL AND SOME OF ITS DERIVATIVES

VII. POTENTIOMETRIC TITRATION OF SOME INTERMEDIATES AND AZO DYES OF THE NAPHTHALENE SERIES

V. V. Perekalin

In our research on the reactions of sulfo acids of 1,5-aminonaphthol with diazo compounds [1], we investigated numerous azo dyes* by the method of potentiometric titration with a glass electrode. Certain regularities of behavior pattern noticed in these substances led us to extend our investigation to cover other naphthalene intermediates and azo dyes.

Very little use has been made of the potentiometric titration method in the study of properties of organic substances [2,3], though B.A.Porai-Koshits and I.V.Grachev [4,5] have recently employed it with success in their investigation of the structure of diazo compounds.

As for the electrolytic dissociation constant of naphthalene compounds, they are known only for a very limited number of naphthalene derivatives: 2-naphthol [6]; 1- and 2-naphthylamines [7]; 1,4- and 1,5-naphthylenediamines [8]; 1- and 2-naphthoic acids [9]; 2-naphthalenesulfo acid [10]; and 1,2-, 1,4-, and 1,5-naphthylaminesulfo acids [11]. The hydrogen-ion concentrations have also been determined for some naphthalene azo dyes. This exhausts the information in the literature available to us during our research.

Our research had as its objective tracing the changes in the dissociation constants of various functional groups (hydroxyl, amino, and sulfo groups) that take place when the structure of these compounds is changed, as well as determining the singularities of their fine structure, if possible.

1. Potentiometric Titration Procedure and Method of Computing Dissociation Constants

The measurement apparatus was like that described in detail in the papers by I.V.Grachev [12]; the only change being that we used the lamp pH meter designed by the State Institute of Applied Chemistry [13] in potentiometric (or, more precisely, acidimetric) titration.

Weighed samples of the substance (about 0.003 mole) were dissolved in 100 ml of a titrated solution of 0.1 *N* caustic soda that contained no carbon dioxide. Hence, the solutions contained an excess of free sodium hydroxide (about 10 ml), the remainder being bound by the substance (hydroxyl and sulfo groups). Then 20 ml of the solution was titrated, with mechanical stirring, with a 0.1 *N* solution of hydrochloric acid of known titer in a current of air, freed from carbon dioxide. In some cases, the solution (or suspension) of the substance, containing an excess of the acid, was back-titrated with a sodium hydroxide solution.

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*A forthcoming report will describe the synthesis of the azo dyes.

The voltmeter was read after each 1 ml of the hydrochloric acid solution was added, as well as after the addition of each 0.5 ml and even each 0.25 ml of hydrochloric acid in the neighborhood of a potential jump and during the jump itself. The rate at which the hydrochloric acid was added was governed by the time required for the galvanometer needle to come to rest.

The pH rose spontaneously during the titration of some compounds, due to the deposition of the substances being titrated in the precipitate. When this happened, we waited (up to 30 minutes) until the changes in the galvanometer readings ceased. We also waited from 5 to 10 minutes whenever a spontaneous increase in the pH was expected during the titration of any substance. The equivalence points on the titration curves were determined graphically, by the method of normals [14], as a rule, as well as by means of differential curves and by the method of derivatives [15]. All three methods yielded results that were in agreement within the limits of experimental error (the second method exhibiting some divergences at times).

The pH of the titration curves was determined from the characteristic of the electrode; this was checked before the beginning of measurements. The theoretical equivalence points were calculated from the stoichiometric equations of the reactions that occur during acidimetric titration. No special computational formulas were derived to compute the dissociation constants of the functional groups of the naphthalene derivatives investigated,[*] the calculation methods set forth in the literature being used, notwithstanding the degree of inaccuracy involved.

Titration of all the substances tested may be classified under a few basic headings:

1) 1-Naphthalenesulfo acid (Fig. 1) is a strong acid (the literature gives a value of 10^{-1} for the k_S[**] of 2-naphthalenesulfo acid [11]), approaching hydrochloric acid in strength, so that it is hard to determine the precise value of its k_S from the titration data [16].

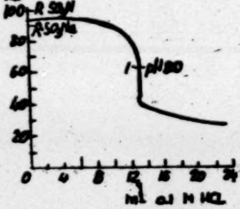

Fig. 1. Titration curve of 1-naphthalene sulfo acid.

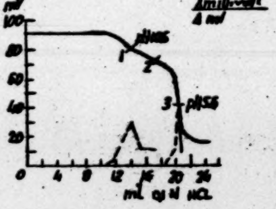

Fig. 2. Titration curve of 1-naphthol.

2) 1-Naphthol (Fig. 2) may be regarded as a weak acid, the computation boiling down to calculating the dissociation constant of a weak acid [16]. The dissociation constant of the hydroxyl group is calculated from the following formulas:

---

[*] As a rule the dissociation constants were computed in each case from the results of 5 to 10 titrations.

[**] The acidity constants of the sulfo and hydroxyl groups, the basicity constants of the amino group, and the dissociations of the water are denoted by k_S, k_{OH}, k_{NH_2}, and k_{H_2O} respectively.

(1) $$k_{OH} = \frac{(H)^2 C}{k_{H_2O}} , \qquad (I)$$

(2) $$k_{OH} = (H), \qquad (II)$$

(3) $$k_{OH} = \frac{(H)^2}{C} . \qquad (III)$$

3) 1-Naphthol-4-sulfo acid (Fig. 3). This case is similar to the titration of a dibasic acid [16]. The k_{OH} at the point (3) is given by the formula:

$$k_{OH} = \frac{(H)^2}{k_S} ;$$

since the sulfo group is highly acid, the calculation may be simplified and performed with the formulas given for calculating the dissociation constant of 1-naphthol.

In computing the dissociation constant of the sulfo group (with some inaccuracy) from the Formulas (I), (II), and (III), we found that the sulfo group in 1-naphthol-4-sulfo acid also retains the properties of a strong acid ($k_S = 10^{-2}$), so that we did not determine the k_S for any of the other sulfo compounds.

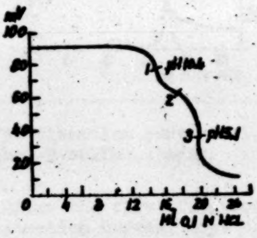

Fig. 3. Titration curve of the sodium salt of 1-naphthol-4-sulfo acid.

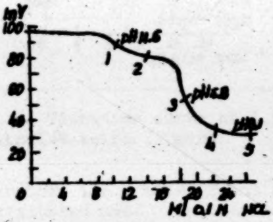

Fig. 4. Titration curve of 1,5-aminonaphthol.

4) 1,5-Aminonaphthol (Fig. 4). The titration of this compound may be regarded as the same as the Bjerrum titration of an ampholyte [17], such as ammonium acetate. According to this point of view, the amino group will be titrated from Points (1) to (3), and the hydroxyl group from (3) to (5). Point (3) will represent an inner salt of 1,5-aminonaphthol. The titration sequence would be the reverse, according to the usual notions. The constants are computed from the following formulas:

(1) $$K_{NH_2} = \frac{K_{H_2O}^2}{(H)^2 S} , \qquad (IV)$$

(2) $$K_{NH_2} = \frac{K_{H_2O}}{(H)} , \qquad (V)$$

$$(3)\quad \frac{K_{OH}}{K_{NH_2}}\ \text{(found)} = \frac{(H)^2}{K_{H_2O}}, \qquad \text{(VI)}$$

$$(4)\quad K_{OH} = (H), \qquad \text{(II)}$$

$$(5)\quad K_{OH} = \frac{(H)^2}{C}. \qquad \text{(III)}$$

5) Aminonaphtholsulfo[illegible] acids and the azo dyes that are derivatives of 1,5-aminonaphtholsulfo[illegible] acids (Figs. 5-18). Since the sulfo group possesses the properties of a strong acid, it may be neglected in our calculations, so that K_S need not be computed, and the computation of the constants for these compounds may be reduced to the sole case of 1,5-aminonaphthol.

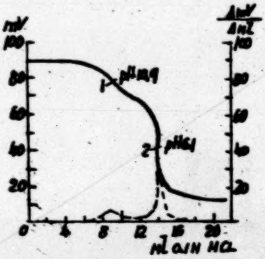

Fig. 5. Titration curve of 1,5-amino-naphthol-2-sulfo[illegible] acid.

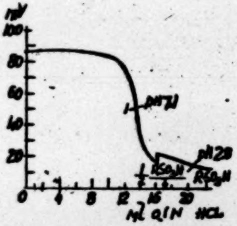

Fig. 6. Titration curve of 1,5-amino-naphthol-4-sulfo[illegible] acid.

After the first function group had been titrated, i.e., after Point (3) on the titration curves, most of the compounds precipitated out.* In these cases, we could not calculate k_{OH} from Formulas (II) and (III), and the k_{OH} was determined from Formula (VI). Whenever the substance remained in solution until the

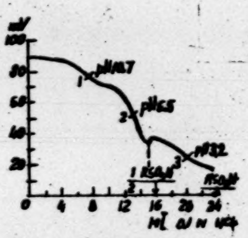

Fig. 7. Titration curve of 1,5-amino-naphthol-6-sulfo[illegible] acid.

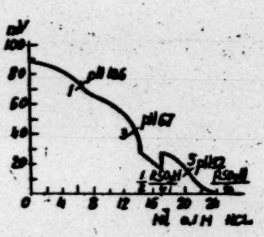

Fig. 8. Titration curve of 1,5-amino-naphthol-7-sulfo[illegible] acid.

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*Owing to the slight solubility of the substances tested, we were frequently unable to prevent the appearance of a precipitate by lowering their concentrations.

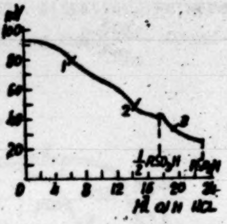

Fig. 9. Titration curve of 1,5-aminonaphthol-8-sulfonic acid.

1) pH 10.6; 2) pH 6.8; 3) pH 3.5

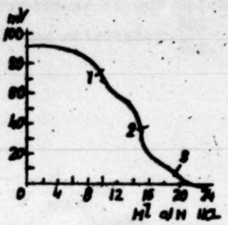

Fig. 10. Titration curve of 2,8-aminonaphthol-6-sulfonic acid.

1) pH 10.2; 2) pH 6.3; 3) pH 2.8

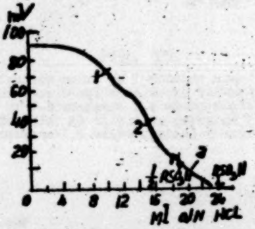

Fig. 11. Titration curve of 2,5-amino-inonaphthol-7-sulfonic acid.

1) pH 10.2; 2) pH 6.4; 3) pH 3.2

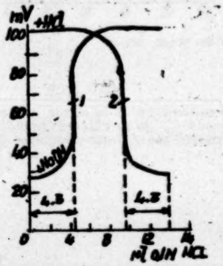

Fig. 12. Titration curve of 2-benzeneazo-1-naphthol.

1) pH 6.9; 2) pH 6.9

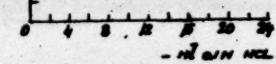

Fig. 13.

1) Titration curve of 4-benzeneazo-1,5-aminonaphthol-2-sulfo acid; 2) titration curve of 8-benzeneazo-1,5-aminonaphthol-2-sulfo acid.

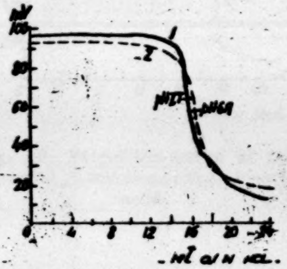

Fig. 14.

1) Titration curve of 2-benzeneazo-1,5-aminonapthol-4-sulfo acid; 2) titration curve of 8-benzeneazo-1,5-aminonaphthol-4-sulfo acid.

end of the titration, we were able to check the correctness of our calculations by comparing the $\frac{K_{OH}}{K_{NH_2}}$ found from Formula (VI) with the calculated $\frac{K_{OH}}{K_{NH_2}}$.

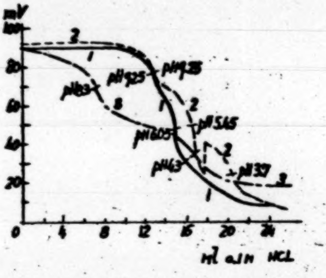

Fig. 15.

1) Titration curve of 2-benzene azo-1,5-aminonapthol-6-sulfo acid; 2) titration curve of 8-benzeneazo-1,5-aminonaphthol-6-sulfo acid; 3) titration curve of 2,8-dibenzeneazo-1,5-aminonaphthol-6-sulfo acid.

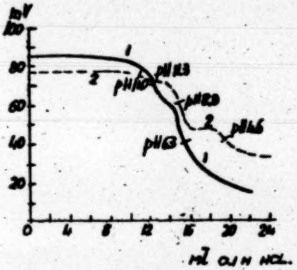

Fig. 16

1) Titration curve of 2-benzeneazo-1,5-aminonaphthol-7-sulfo acid; 2) titration curve of 6-benzeneazo-1,5-aminonaphthol-7-sulfo acid.

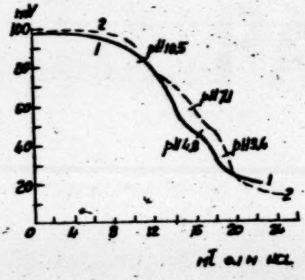

Fig. 17.

1) Titration curve of 2-benzeneazo-1,5-aminonaphthol-8-sulfo acid; 2-titration curve of 6-benzeneazo-1,5-aminonaphthol-8-sulfo acid.

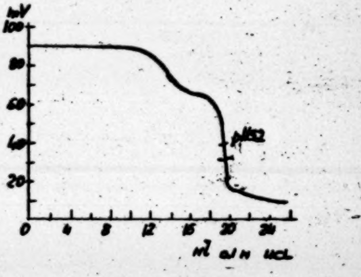

Fig. 18. Titration curve of 2-benzeneazo-1,5-aminonaphthol-4-sulfo acid.

According to Bjerrum, the calculated constants of 1,5-aminonaphthol, its sulfo acids, and the azo dyes produced from these sulfo acids as described in Section 4, are the true constants.

They differ greatly, however, from the values found in the literature and from the constants computed by us for substances that are not ampholytes (1-naphthol, 1-naphthylamine, 1-naphthalene-4-sulfo acid) though their structures are close to those of our ampholytes.

To retain uniformity in the values of the constants we used Bjerrum's equation [17,18], which makes it possible to pass from the true constants to the apparent ones:

$$k_{H_2O} = K_{NH_2} \cdot k_{OH} = K_{OH} \cdot k_{NH_2} , \qquad \text{(VII)}$$

where K_{NH_2} and K_{OH} are the true basic and acid constants, and
k_{OH} and k_{NH_2} are the apparent basic and acid constants.

The apparent constants were computed for all the ampholytes tested (1,5-aminonaphthol, the aminonaphtholsulfo acids, and the azo dyes prepared from the 1,5-aminonaphtholsulfo acids); their order of magnitude was close to those of the constants of the nonampholytes listed above (1-naphthol, etc.). We therefore based all our conclusions regarding the relationship between the values of the constants and the structure of the ampholytes upon the apparent constants and employed the usual concepts of the titration sequence of functional groups in our evaluation of the titration curves.

II. Description of the Titration Curves

Titration of 1-naphthalenesulfo acid (Fig. 1) yields a curve that exhibits an equivalence point corresponding to the titration of the free sodium hydroxide remaining after the formation of the sodium salt of the sulfo acid; the salt itself does not produce a potential jump.

The first two potential jumps of the curves for 1-naphthol, 1-naphthol-4-sulfo acid, and 1,5-aminonaphthol and its sulfo acids (Figs. 2-11) represent the titration of the sodium hydroxide and the naphtholate. The sulfo group of 1-naphthalene-4-sulfo acid does not cause a third jump. The third slight bend in the 1,5-aminonaphthol curve is due to the formation of a hydrochloride. The third bend in the curves of the 1,5-aminonaphtholsulfo acids may be attributed to the sulfo group; the free sulfo acid forms an inner salt with the amino group as soon as the former is produced, the salt precipitating out because of its low solubility. Hence the amino group is titrated together with the sulfo group, the titration of both groups being covered by one section of the curve. When a fourth equivalent of hydrochloric acid is added, the inner salt is titrated, but we were unable to detect a fourth potential jump.

The 1-naphthol and the 1,5-aminonaphthol precipitate out after the former has been converted into a naphthol from a naphtholate, and 0.75 equivalent of the hydroxyl group has been back-titrated in the latter,* 1-naphthol-4-sulfo acid and 1,5-aminonaphthol-2-sulfo acid remaining in solution. All the other sulfo acids of 1,5-aminonaphthol (the 4-, 6-, 7-, and 8-sulfo acids) are precipitated (half of the weighed sample) after half of the sulfo group equivalent has been back titrated. The pH rises spontaneously at the same time (Figs. 6-9) owing to the sharp drop in the hydrogen ion concentration in the solution.

The subsequently investigated 2,8-aminonaphthol-6-sulfo acid – gamma acid (Fig. 10) – and 2,5-aminonaphthol-7-sulfo acid – J-acid (Fig. 11) – behave differently: the former remains in solution, its curve displaying three potential jumps, while the latter precipitates out.

The para hydroxy azo dyes – derivatives of 1-naphthol and 1,5-aminonaphthol –

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*If the solution of 1,5-aminonaphthol is diluted tenfold, the precipitate appears when the same quantity of hydrochloric acid is added as when there is no dilution.

are precipitated during titration after about half an equivalent of the hydroxyl group has been back-titrated, so that it was impossible to compute any precise values for their dissociation constants.

The curve of the o-hydroxy azo dye prepared from 1-naphthol, which is insoluble in dilute alkalies and was investigated in alcoholic alkaline solutions, exhibited one potential jump, corresponding to the titration of all the sodium hydroxide in the sample (Fig. 12). Hence, in this o-hydroxy azo dye the hydroxyl group is not titrated and does not form naphtholates, apparently because of the formation of a hydrogen bond between the hydroxyl hydrogen atom and the nitrogen atom in the azo group [1].

The titration of the azo dyes - derivatives of the sulfo acids of 1,5-aminonaphthol (Figs. 14-17) took place as follows: the curves of the amino azo dyes did not have any first or third potential jump (in some instances, such as Figs. 13, 14, and 16, the first jump was shifted to the second bend), and the dyes themselves remained in solution or were precipitated as their sodium salts. Therefore, the amino azo dyes and the original sulfo acids are titrated differently. The general character of titration and the shape of the curves of the hydroxy azo dyes are the same as those of the original sulfo acids.

Thus, the difference in behavior during potentiometric titration reveal differences in the properties (such as solubility) of compounds of similar structure.

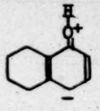
III. Evaluation of Research Results

The ability of the hydroxyl group in 1-naphthol to dissociate, i.e., its slightly acid properties ($k_{OH} = 2.5 \cdot 10^{-10}$)* or the mobility of the hydrogen atom, may be attributed to the shift of the unshared pair of electrons in the oxygen atom of the hydroxyl group to the ring, resulting in the appearance of an electron gap (II) in the oxygen atom, which tries to be filled at the expense of the electron pair in the H—O bond; this results in the ionization of the hydrogen atom. It must be assumed that the percentage of (II) ions is negligible, since the acidity constant of 1-naphthol is small:

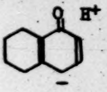
TABLE 1

Dissociation Constants

Test No.	Substance	k_{OH}	k_{NH_2}
1	1,5-Aminonaphthol	$5 \cdot 10^{-11}$	$1.4 \cdot 10^{-10}$
2	1-Naphthol	$2.5 \cdot 10^{-10}$	–
3	1-Naphthol-4-sulfo acid.	$3 \cdot 10^{-9}$	–
4	1,5-Aminonaphthol-2-sulfo acid	$2.5 \cdot 10^{-10}$	$3 \cdot 10^{-13}$
5	1,5-Aminonaphthol-4-sulfo acid	$2 \cdot 10^{-12}$	$2.3 \cdot 10^{-12}$
6	1,5-Aminonaphthol-7-sulfo acid	10^{-9}	$2 \cdot 10^{-10}$
7	1,5-Aminonaphthol-6-sulfo acid	10^{-8}	$7.4 \cdot 10^{-11}$
8	1,5-Aminonaphthol-8-sulfo acid	$2 \cdot 10^{-9}$	$6 \cdot 10^{-10}$
9	2,8-Aminonaphthol-6-sulfo acid	$2 \cdot 10^{-9}$	$4.7 \cdot 10^{-11}$
10	2,5-Aminonaphthol-7-sulfo acid...........	$2 \cdot 10^{-3}$	$9 \cdot 10^{-11}$



(I)



(II)

The acidity constant of the hydroxyl group in 1,5-aminonaphthol ($k_{OH} = 5 \cdot 10^{-11}$) is lower than that of 1-naphthol, since the shift of the unshared electron pair in the hydroxyl group to the ring is hampered by the fact that the unshared electron pair in the amino group likewise tries to migrate to the ring (I), thus setting up a higher electron density at the carbon atom to which the hydroxyl group is attached, and diminishing the ability of the hydrogen atom to dissociate.

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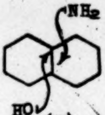
* The acidity constants of the hydroxyl group and the basicity constants of the amino group are listed in Table 1 for the intermediates and in Table 2 for the dyes.

The basicity constant of the amino group in 1,5-aminonaphthol ($k_{NH_2} = 1.4 \cdot 10^{-11}$) is higher than that of 1-naphthylamine ($k_{NH_2} = 9.9 \cdot 10^{-10}$), for the unshared electron pair in the hydroxyl group, increasing the electron density of the carbon atom to which the amino group is attached, increases its basicity:



(I)

The increase in the acidity of the hydrogen atom in the hydroxyl group, due to the presence of the sulfo group in the para position to it (compare the acidity constant of 1-naphthol with the $k_{OH} = 3 \cdot 10^{-9}$ of 1-naphthol-4-sulfo acid), may be explained by the greater effort of the unshared pair in the hydroxyl group to move over to the ring than is the case in the 1-naphthol:

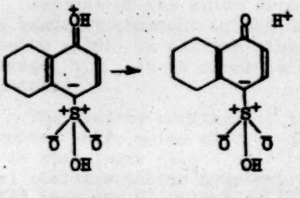


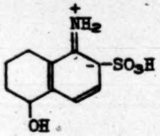
TABLE 2

Dissociation Constants

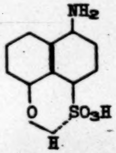
Test No.	Azo dyes	k_{OH}	k_{NH_2}
1	4-Benzeneazo-1,5-aminonaphthol-2-sulfo acid..........	$4 \cdot 10^{-12}$	$3.3 \cdot 10^{-9}$
2	8-Benzeneazo-1,5-aminonaphthol-2-sulfo acid	$2 \cdot 10^{-10}$	$1.2 \cdot 10^{-10}$
3	2-Benzeneazo-1,5-aminonaphthol-4-sulfo acid..........	$2.5 \cdot 10^{-12}$	$7.4 \cdot 10^{-11}$
4	8-Benzeneazo-1,5-aminonaphthol-4-sulfo acid	$1.6 \cdot 10^{-11}$	$4 \cdot 10^{-11}$
5	2-Benzeneazo-1,5-aminonaphthol-7-sulfo acid	$2.5 \cdot 10^{-10}$	$7.4 \cdot 10^{-12}$
6	6-Benzeneazo-1,5-aminonaphthol-7-sulfo acid	$4 \cdot 10^{-11}$	$3 \cdot 10^{-9}$
7	2-Benzeneazo-1,5-aminonaphthol-6-sulfo acid	$1.6 \cdot 10^{-8}$	$1.4 \cdot 10^{-11}$
8	8-Benzeneazo-1,5-aminonaphthol-6-sulfo acid..........	$1.3 \cdot 10^{-8}$	$2 \cdot 10^{-10}$
9	2,8-Dibenzeneazo-1,5-aminonaphthol-6-sulfo acid	$5 \cdot 10^{-7}$	$7 \cdot 10^{-12}$
10	2-Benzeneazo-1,5-aminonaphthol-8-sulfo acid	10^{-8}	$4.6 \cdot 10^{-13}$
11	6-Benzeneazo-1,5-aminonaphthol-8-sulfo acid	$1.6 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$
12	2-Benzeneazo-1-naphthol-4-sulfo acid	$1.6 \cdot 10^{-9}$	–

Turning to the constants of the sulfo acids of 1,5-aminonaphthol, we find that the acidity constant of the hydroxyl group in 1,5-aminonaphthol-2-sulfo acid ($k_{OH} = 2.5 \cdot 10^{-10}$) is the same as the k_{OH} of naphthol, apparently due to the fact that 1) the sulfo group does not increase the acidic properties of the hydroxyl group, inasmuch as its location does not allow it to exert any direct influence upon the mobility of the unshared electron pair of the hydroxyl group, while its induction effect is negligible owing to its distance from the hydroxyl group; and 2) the amino group cannot diminish the acidity of the hydroxyl group appreciably, since its own unshared electron pair is blocked owing to its interaction with the sulfo group.

Therefore, the mobility of the hydrogen atom in the hydroxyl group of this sulfo acid (as in the case of 1-naphthol) is largely governed by the interaction of the hydroxyl group with the ring:



The sharp drop in the k_{OH} of the hydroxyl group in 1,5-aminonaphthol-4-sulfo acid, compared to the constants of the other aminonaphtholsulfo acids may, apparently, be due to the blocking action of the sulfo group:



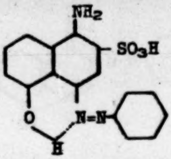
In the other sulfo acids of this series – the 6-, 7-, and 8-sulfo acids, as well as 2,8-aminonaphthol-6-sulfo acid and 2,5-aminonaphthol-7-sulfo acid – the dissociation constant of the hydroxyl group (10^{-9}) is the same as the k_{OH} of 1-naphthol-4-sulfo acid.

Hence, the sulfo group attached to the same ring as the hydroxyl group increases the latter's dissociation constant over the value found in naphthol or in 1,5-aminonaphthol, owing to direct interaction with that group or by induction, as is also the case in 1-naphthol-4-sulfo acid.

As for the basicity constant of the amino group in the sulfo acids of 1,5-aminonaphthol, the negligible value of this constant in 1,5-aminonaphthol-2-sulfo acid ($k_{NH_3} = 3 \cdot 10^{-13}$) compared to its value in 1,5-aminonaphthol ($k_{NH_3} = 10^{-11}$) may be due to the fact that the adjacent sulfo group lowers the activity of the amino group's unshared electron pair considerably.

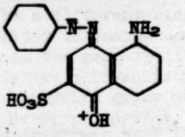
Removal of the sulfo group to a greater distance results in an increase in the basicity constant of the amino group; $k_{NH_3} = 2.3 \cdot 10^{-12}$ in 1,5-aminonaphthol-4-sulfo acid. In all the other sulfo acids of this series, $k_{NH_3} = 10^{-10}$ on the average, i.e., it is close to the value of the basicity constant in 1,5-aminonaphthol.

The acidity constant of the hydroxyl group in the amino azo dyes derived from the sulfo acids of 1,5-aminonaphthol follows a different behavior pattern: it is much lower ($k_{OH} = 4 \cdot 10^{-12}$) in the dye that contains an azo group in the peri position to the hydroxyl group (4-benzeneazo-1,5-aminonaphthol-2-sulfo acid) than the $k_{OH} = 2.5 \cdot 10^{-10}$ of the original sulfo acid, apparently because of the blocking action of the azo group:



The k_{OH} of the o-amino azo dyes is no different or only slightly higher than the constants of the original sulfo acids.

The p-hydroxy azo dyes, as a rule, have a higher acidity constant of their hydroxyl group than the k_{OH} of the parent aminonaphthol sulfo acids, apparently because of the interaction between the hydroxy and azo groups, which results in a shift of the hydroxyl group's unshared electron pair to the azo group:



8-Benzeneazo-1,5-aminonaphthol-6-sulfo acid, for instance, has a $k_{OH} = 1.3\cdot 10^{-8}$ (the $k_{OH} = 10^{-9}$ in the original sulfo acid).

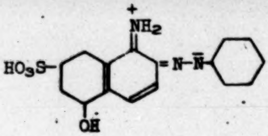
In the disazo dye systhesized from the same sulfo acid, the azo group in the para position to the hydroxyl group increases the latter's constant above that of the original monoamino azo dye.

By analogy with the ortho azo dyes synthesized from 1-naphthol, the hydroxyl group in ortho hydroxy azo dyes synthesized from 1,5-aminonaphthol-7- and -8-sulfo acids and from 1-naphthol-4-sulfo acid: 6-benzeneazo-1,5-aminonaphthol-7-sulfo acid (I), 6-benzeneazo-1,5-aminonaphthol-8-sulfo acid (II), and 2-benzeneazo-1-naphthol-4-sulfo acid (III), ought not to be able to be titrated either, because of the establishment of a hydrogen bond between the hydroxyl hydrogen atom, and the azo group [1,19,20]. It can be titrated in these dyes, however, though in (I) $k_{OH} = 4\cdot 10^{-11}$ is lower, and in (II) and (III) $k_{OH} = 1.6\cdot 10^{-9}$ remains unchanged, as against the constants of the original sulfo acids.

This apparent contradiction may be explained by the fact that the sulfo group increases the acidic properties (the mobility) of the hydrogen atom in the hydroxyl group, thus rupturing the hydrogen bond and therefore impairing its stabilizing action. We have observed a similar rupture of a hydrogen bond by the action of a sulfo group in peri-hydroxy azo dyes that are derivatives of 2,8-aminonaphthol-5- and -7- sulfo acids [21].

The basicity constants of the amino groups in ortho amino azo dyes is usually lower than the constants in the original amino sulfo acids and hydroxy azo dyes ($k_{NH_2} = 7.4\cdot 10^{-12}$ in the ortho amino azo dye derived from 1,5-aminonaphthol-7-sulfo acid, whereas $k_{NH_2} = 1.8\cdot 10^{-10}$ in the original sulfo acid, and $k_{NH_2} = 3\cdot 10^{-9}$ in the ortho hydroxy isomer).

The introduction of a second azo group into the molecule of a mono-hydroxy azo dye at the ortho position to the amino group likewise diminishes the latter's constant. This decrease in the basicity constant may be explained as due to the stabilizing effect of the azo group upon the activity of the amino group's unshared electron pair:



This research has discovered the following rules governing the changes in the dissociation constants of the compounds tested: 1) the amino group diminishes the acidity constant of the hydroxyl group in 1,5-aminonaphthol below the value for 1-naphthol, whereas the hydroxyl group increases the basicity constant of the amino group in 1,5-aminonaphthol above that for 1-naphthol; 2) 1-naphthalene sulfo acid is as strong an acid as hydrochloric acid; 3) in 1-naphthol- and 1,5-aminonaphtholsulfo acids, the sulfo group attached to the same ring as the hydroxyl group increases the mobility of the latter's hydrogen atom, whereas the the sulfo group attached to a different ring than the hydroxyl group of 1,5-aminonaphthol has no essential influence upon the latter's dissociation constant. The sulfo (and azo) group in the peri position to the hydroxyl group in 1,5-aminonaphthol lowers the latter's dissociation constant considerably. In the 1,5-aminonaphtholsulfo acids, the sulfo group attached to the same ring as the amino group lowers the latter's basic properties. Shifting the sulfo group to another ring destroys its stabilizing effect upon the amino group; 4) in the para hydroxy azo dyes, the azo group increases the mobility of the hydrogen atom in the hydroxyl group. The hydroxyl group is not titrated in the ortho hydroxy azo dyes. Whenever these dyes have the sulfo group attached to the same ring as the hydroxyl group, the latter is titrated in the usual manner. In the ortho amino azo dyes, the azo group diminishes the basic properties of the amino group. A second azo group (in disazo dyes) reinforces the effect of the first group.

SUMMARY

1. It has been found that the method of potentiometric titration with a glass electrode is serviceable in studying the comparative effect of various substituents (sulfo and azo groups) upon the acidity (hydrogen atom mobility) of the hydroxyl group and upon the basicity of the amino group.

2. Potentiometric titration makes it possible to disclose the fine-structure features of various naphthalene derivatives.

3. It has been shown that a sulfo group in the para position to a hydroxyl group ruptures the hydrogen bond in the ortho hydroxy azo dyes of the naphthalene series.

4. In this research project 28 substances have been investigated for the first time by the method of potentiometric titration, the dissociation constant being calculated for the first time for 22 of them.

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*See CB translation p. 985 ff.

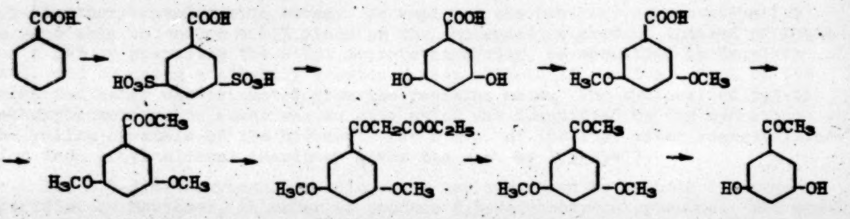
**See CB translation p. 1255 ff.

THE ABSORPTION SPECTRA AND STRUCTURES OF BENZENE DERIVATIVES

XVI. 3,5-DIHYDROXY- AND 3,5-DIMETHOXYACETOPHENONE

N. A. Valyashko and A. E. Lutsky

We synthesized 3,5-dihydroxy- and 3,5-dimethoxyacetophenone by means of the following series of chemical changes:



3,5-Disulfobenzoic acid was prepared by heating benzoic acid with oleum containing 50 or 70% of the free anhydride (Barth and Senhofer [1], Hohenemser [2], Graves and Adams [3]). Burner [4] simplified the synthesis of this acid considerably by suggesting that sulfonation be done in an open flask, reacting benzoic acid dissolved in 50% oleum with chlorosulfonic acid or anhydrous HCl gas. In view of the fact that monosulfobenzoic acid, according to Offermann [5], is readily formed by heating benzoic acid with 10-20% oleum, the synthesis of 3,5-disulfobenzoic acid could be simplified still further by substituting 10-13% of oleum for the 50% oleum in Bruner's method. Sulfonation was effected as follows: 50 g of benzoic acid was heated for 30 minutes to 220° with 250 g of 13% oleum, after which 100 g of chlorosulfonic acid was added in two batches of 50 g each. The reaction mixture was heated to 250° for 1.5 hours over an oil bath after the addition of each batch. The mixture was then neutralized with $BaCO_3$ and filtered, the filtrate being evaporated and acidulated with hydrochloric acid. The yield of light-yellow crystals of the barium acid salt of 3,5-disulfobenzoic acid was 79% of the theoretical.

3,5-Dihydroxybenzoic acid was prepared from the barium acid salt of 3,5-disulfobenzoic acid by fusing the latter with caustic potash as specified by Graves and Adams [3] and N.A.Valyashko and M.M.Shcherbak [6]. The yield was 65-70% of the theoretical. The synthesized 3,5-dihydroxybenzoic acid fused with decomposition at 238-239° after recrystallization from water (the melting points given in the literature vary over a fairly wide range, viz.: from 220 to 240°; cf Barth and Senhofer [1], Sabalitschka [7], Hopfgartner [8], Böttinger [9], Herzig and Epstein [10], etc.). The acid exhibited all its characteristic reactions, namely: ,anthrachrysone with sulfuric acid; decolorizing a $KMnO_4$ solution in the cold; and no color reaction with $FeCl_3$ (Barth and Senhofer [11], Bullow and Riess [12], Tiemann and Parisius [13], and Lesser and God [14]).

We prepared 3,5-dimethoxybenzoic acid from the 3,5-hydroxy acid by methylating the latter with dimethyl sulfate as specified by Bullow and Riess [12] and by Mauthner [15]. The yield was quantitative. After recrystallization from alcohol the 3,5-dimethoxybenzoic acid consisted of elongated white needles with a m.p. of 181-183° (the literature gives 180-181°, according to Mauthner [15] and Solway [16]; 182°, according to Richter [17], and 185-186°, according to Herzig and Epstein [10]).

The methyl ester of 3,5-dimethoxybenzoic acid was prepared by heating a mixture of 3,5-dimethoxybenzoic acid (desiccated with calcined potash), methanol, and concentrated sulfuric acid for 6 hours with a reflux condenser. The yield of the ester (the 287-290° fraction was selected) totaled 90%. The resulting oil solidified upon standing into yellow crystals, which fused at 38° after a single recrystallization from ligroin (the m.p. is 41-42° according to Bullow and Riess [12] and Kaufmann and Kieser [18]).

The resultant ester was condensed with ethyl acetate in order to secure the 3,5-dimethoxybenzoicacetic ester. We employed the Mauthner condensation [19]. We were able to secure a 43% yield of the condensation product instead of Mauthner's 34% by preparing the ethyl acetate carefully, as specified by Krapivin [20], and by using a slightly greater excess of metallic sodium. Part of the unreacted ester was extracted from the reaction mass. The synthesized 3,5-dimethoxybenzoicacetic ester was an oil, which was identified by its hydrazone. The yellow crystals of the hydrazone had a m.p. of 154-155° after recrystallization from ethyl alcohol (Mauthner gives the m.p. as 153-154°).

The 3,5-dimethoxybenzoicacetic ester was subjected to ketonic cleavage as specified by Mauthner, in order to produce 3,5-dimethoxyacetophenone. The synthesized product was purified by vacuum fractionation, the fraction distilling at 143-146° (8-9 mm) being selected; the b.p. is given as 151-152° (10 mm) in the literature. The colorless thick liquid solidified into snow-white crystals upon cooling; the m.p. was 41-42° after recrystallization from petroleum ether. The crystals are freely soluble in alcohol, and less so in hexane.

The 3,5-dimethoxyacetophenone was demethylated by heating it with chlorobenzene and aluminum chloride, as specified by Mauthner [22], in order to secure 3,5-dihydroxyacetophenone. The ketone was recrystallized from water; elongated white needles with a m.p. of 147-148°, sparingly soluble in water or hexane, though readily soluble in ethyl alcohol.

Spectrographic investigations. N.A.Valyashko and M.M.Shcherbak [6] have investigated the absorption spectra of 3,5-dihydroxybenzaldehyde in various media, finding that it can exist in two equilibrium states, α and φ , exhibiting a spectrum of the α-type. They also established a link between the absorption spectra of 3,5-dihydroxy- and 3-hydroxybenzaldehyde.

In the present research the analog of 3,5-dihydroxybenzaldehyde – 3,5-dihydroxyacetophenone – was analyzed spectrographically to check the general validity of the relationships previously established. The spectra of 3,5-dihydroxyacetophenone were recorded in ethyl alcohol with various amounts of HCl and sodium alcoholate present, and in concentrated and dilute sulfuric acid. 3,5-Dimethoxyacetophenone was investigated in the same solvents, as well as in hexane. These are the first spectrographic investigations ever made of these two substances.

3,5-Dihydroxyacetophenone in ethyl alcohol. The negligible solubility of

3,5-dihydroxyacetophenone in hexane made it impossible to investigate its spectrum in hexane. Its spectra in ethyl alcohol were recorded at the following concentrations: 10^{-2}, 10^{-3}, 10^{-4}, and $2\cdot10^{-5}$ mol.

The absorption curve (Table 1 and Fig. 1, Curve 2) starts at $\varepsilon = 10$ and $\lambda = 3900$ A, rising with a slight slope toward the shorter wavelengths. The curve exhibits a slight bend in the region between $\lambda = 3840$ and 3760 A and $\varepsilon = 25$-50. The curve begins to round off at $\varepsilon = 4000$, constituting a band with a maximum at $\lambda = 3210$ A and $\varepsilon = 5000$. Then the curve drops to a minimum at $\lambda = 2985$ A and $\varepsilon = 1600$, and, rising again, forms a second band with a maximum at $\lambda = 2650$ A and $\varepsilon = 10000$. There is a clearly marked bend on the longwave side of this band, between 2930-2790 A and $\varepsilon = 2500$-4000, evidence of the existence of another band that is not manifested because of the superposition upon it of the band with a maximum at $\lambda = 2650$ A. There is a third, very strong, band with a maximum at $\lambda = 2180$ A and $\varepsilon = 25000$, in the shortwave section of the curve. The minimum separating the last two bands is located at $\lambda = 2410$ A and $\varepsilon = 1300$.

TABLE 1

3,5-Dihydroxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol. in alcohol

λ		ε
3900		10
3260		4000
3210	maximum	5000
3160		4000
3010		2000
2985	minimum	1600
2960		2000
2790	bend	4000
2680		8000
2650	maximum	10000
2620		8000
2430		1600
2410	minimum	1300
2390		1600
2190		20000
2180	maximum	25000
2170		20000
2140		15000

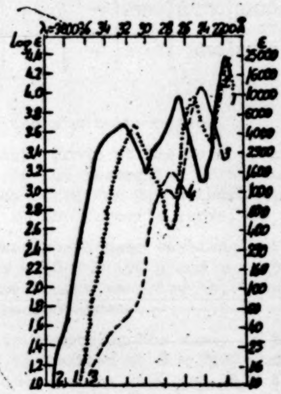


Fig. 1.

1) 3-hydroxyacetophenone 10^{-2} - $2\cdot10^{-5}$ mol., in alcohol; 2) 3,5-dihydroxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol., in alcohol; 3) acetophenone in alcohol; 4) peak of the φ-band of phenol in alcohol.

The data on the absorption band maximu of 3-hydroxyacetophenone [23] and 3,5-dihydroxyacetophenone in alcohol are justaposed in Table 2. The table also lists the data on the band maxima of acetophenone in alcohol (according to N.A.Valyashko and Yu.S.Rozum [24], benzaldehyde (according to Henry [25]), and 3-hydroxy- and 3,5-dihydroxybenzaldehyde (according to N.A.Valyashko and M.M.Shcherbak [6]).

Inspection of the figures in Table 2, together with the absorption curves for 3-hydroxy- and 3,5-dihydroxyacetophenone (Fig. 1, Curves 1 and 2), indicates that their spectra are of the same type. In both instances, the curves consist of the same three bands, that is, the bands with maxima at $\lambda = 3210$, 2650, and 2180 A, which may be regarded as the somewhat displaced α_2-, α_1-, and α_1'- bands, respectively, of 3-hydroxyacetophenone. In the longwave region of the spectrum the 3,5-dihydroxyacetophenone curve is nearly parallel to that of 3-hydroxyaceto-

TABLE 2

Compound	α_2'-band		α_2''-band		φ-band		α_1-band		α_1'-band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
Acetophenone in alcohol	3210	50	–	–	2770	1000	2420	12500	1990	20000
3-Hydroxyacetophenone in alcohol	–	–	3110	5000	–	–	2525	1000	2180	25000
3,5-Dihydroxyacetophenone in alcohol	–	–	3210	5000	Bend between 2960-2790	2500-4000	2650	10000	2180	25000
Benzaldehyde in alcohol	3280	20	–	–	2805	1630	2440	16260	–	–
3-Hydroxybenzaldehyde in alcohol	–	–	3180	3500	–	–	2550	10000	2200	20000
3,5-Dihydroxybenzaldehyde in alcohol	–	–	3340	3500	–	–	2710	9000	2200	15000

phenone, while the two curves almost coincide in the shortwave region.

It follows that introducing a second hydroxyl group at the meta position to the carbonyl group causes no essential change in the absorption of the initial 3-hydroxyacetophenone. Still, the absorption curve for 3,5-dihydroxyacetophenone does exhibit a few differences, compared to the former's curve, to wit:

a) The α_2-band is perceptibly shifted toward the longer wavelengths: the longwave edge of this band is shifted 240 A and $\varepsilon = 10$ and 190 A and $\varepsilon = 130$, while the band maximum is shifted 100 A toward the longer wavelengths, though its strength is the same as that in the 3-hydroxyacetophenone.

b) The absorption is shifted, the intensity remaining the same, in the α_1-band as well. The longwave edge of this band is located at $\varepsilon = 2500$ and 4000 at $\lambda = 2930$ and 2790 A in 3,5-dihydroxyacetophenone, and at 2650 and 2630 A, respectively, in 3-hydroxyacetophenone, i.e., 280 and 160 A farther toward the longer wavelengths; the band maximum is shifted toward the longer wavelengths by nearly the same amount as in the α_2''-band, to wit: 125 A. Comparison with the absorption curve of acetophenone shows that the introduction of a second OH group at the meta position gives rise to a further shift of this band toward the longer wavelengths, of about the same magnitude as is caused by the introduction of the first hydroxyl group at the same position. This perceptible shift of the longwave edge of the α_1-band is related to the circumstance that there is a bend at $\varepsilon = 2500$-4000, corresponding to a φ-band shifted somewhat toward the longer wavelengths and noticeably stronger, such as is characteristic of the absorption of phenol (the summit of the φ-band in phenol, as given by Kepianka [28], is shown in Fig. 1). The appreciable rise in the minimum between the α_2''- and α_1-bands is further evidence of the increase in intensity of absorption in the φ-band: the absorption intensity at this minimum in 3,5-dihydroxyacetophenone is four times the value observed for 3-hydroxyacetophenone.

The relationships noted above are quite analogous to those observed by N.A.Valyashko and M.M.Shcherbak [8] for 3,5-dihydroxybenzaldehyde. The introduction of a second OH group into 3-hydroxybenzaldehyde at the meta position to the carbonyl group also causes a shift of the α_2''- and α_1-bands toward the longer wavelengths, the intensity remaining unchanged, while the absorption intensity at the minimum between these two bands is increased, etc.

The figures in Table 2 likewise indicate that the introduction of a second hydroxyl group at the 5-position increases the quantitative difference between the corresponding derivatives of benzaldehyde and acetophenone. Whereas the difference between the locations of the band maxima in 3-hydroxyacetophenone and 3-hydroxybenzaldehyde is 70 A for the α_2"-band and 25 A for the α_1 band, this difference is 130 A and 60 A, respectively, in the 3,5-dihydroxy derivatives.

3,5-Dimethoxyacetophenone in hexane and in alcohol. We investigated 3,5-dimethoxyacetophenone in hexane solutions of the following concentrations: 10^{-2}, 10^{-3}, 10^{-4}, and $2\cdot10^{-5}$ mol. The absorption curve (Table 3 and Fig. 2, Curve 2) starts at $\lambda = 3570$ A and $\varepsilon = 10$ and rises with a slight bend between 3530 and 3490 A and $\varepsilon = 40$-60; after the bend the curve rises steeply, exhibiting a maximum at $\lambda = 3120$ A and $\varepsilon = 8000$. Then the curve drops to a minimum at $\lambda = 2820$ A and $\varepsilon = 1600$, and, rising again, exhibits a stronger band with a maximum at $\lambda = 2590$ A and $\varepsilon = 20000$. The curve exhibits still another strong band in the shortwave region of the spectrum, with a maximum at $\lambda = 2155$ A and $\varepsilon = 30000$. The minimum between these last two bands lies at $\lambda = 2390$ A and $\varepsilon = 3500$.

TABLE 3

3,5-Dimethoxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol, in hexane			3,5-Dimethoxyacetophenone, 10^{-2} - $3\cdot10^{-5}$ mol., in alcohol		
λ		ε	λ		ε
3570		10	3720		10
3530		40	3230		4000
3490	bend	60	3180	maximum	5000
3200		7000	3130		4000
3120	maximum	8000	2940		2000
3040		7000	2900	minimum	1600
2870		2000	2860		2000
2820	minimum	1600	2650		8000
2770		2000	2630	maximum	10000
2620		17500	2610		8000
2590	maximum	20000	2400		1600
2560		17500	2380	minimum	1300
2410		4000	2360		1600
2390	minimum	3500	2190		23300
2370		4000	2185	maximum	25000
2160		25000	2180		23300
2155	maximum	30000	2150		16600
2150		25000			
2130		17500			

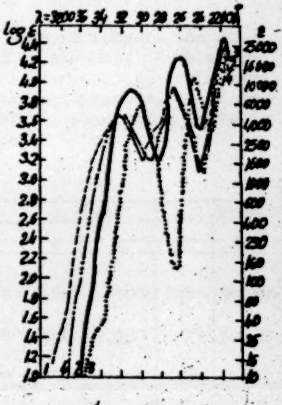


Fig. 2.

1) 3.5-Dihydroxyacetophenone 10^{-2} - $2\cdot10^{-5}$ mol., in alcohol; 2) 3.5-dimethoxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol., in hexane; 3) 3-methoxyacetophenone, 10^{-2} - $4\cdot10^{-5}$ mol., in hexane; 4) 3.5-dimethoxyacetophenone, 10^{-2} - $3\cdot10^{-5}$ mol., in alcohol.

We investigated 3,5-dimethoxyacetophenone in alcohol solutions of the following concentrations: 10^{-2}, 10^{-3}, 10^{-4}, and $3\cdot10^{-5}$ mol. The absorption curve (Table 3 and Fig. 2, Curve 4) begins at $\varepsilon = 10$ and $\lambda = 3720$ A, rising with a slight slope toward the shorter wavelengths and exhibiting its first band with a maximum at $\lambda = 3180$ A and $\varepsilon = 5000$. After a comparatively shallow minimum at $\lambda = 2900$ A and $\varepsilon = 1600$, the curve exhibits a second band with a maximum at $\lambda = 2630$ A and $\varepsilon = 10000$. There is a third band in the shortwave region, with a maximum at $\lambda = 2185$ A and $\varepsilon = 26600$; the minimum between these latter two bands lies at $\lambda = 2380$ A and $\varepsilon = 1300$.

The data on the absorption band maxima of 3-methoxy- and 3,5-dimethoxyacetophenone in hexane and alcohol are listed in Table 4 (the data for 3-methoxyacetophenone have been taken from Report XV [23], together with the data for 3,5-dihydroxyacetophenone in alcohol.

The data in Table 4, together with the absorption curves for 3,5-dimethoxyacetophenone in hexane and in alcohol (Fig. 2, Curves 2 and 4) indicate that the curve has the same shape in alcohol as in hexane: both curves have the same bands, the only thing missing in the alcohol curve being the bend between 3530 and 3490 A observed in hexane. The alcohol curve also exhibits the following differences, compared to the hexane curve:

a) The absorption is shifted somewhat toward the longer wavelengths in all the bands. At $\varepsilon = 10$, for example, the absorption is shifted 150 A toward the longer wavelengths and 100 A at $\varepsilon = 100$; the band maxima are shifted 60, 40, and 30 A; it is only the shortwave edge of the last band that is shifted somewhat toward the shorter wavelengths, compared to the curve in hexane.

b) The intensity is perceptibly less, particularly in the first two bands; the absorption is likewise much less in the region of the minimum between the last two bands.

All these relationships parallel those observed when we compare the absorption curves of 3-methoxyacetophenone in hexane and in alcohol. Here again, the bands in alcohol are shifted more toward the longer wavelengths, their maxima being shifted by the same amount as in 3,5-dimethoxyacetophenone, viz.: 60, 30, and 40 A, respectively; in alcohol the intensity of the absorption bands is much lower, as was the case in 3,5-dimethoxyacetophenone.

TABLE 4

Compound	α_2'-band		α_2''-band		α_1-band		α_1'-band	
	λ	ε	λ	ε	λ	ε	λ	ε
3-Methoxyacetophenone in hexane	~ 3250	~ 50	3025	6000	2460	12500	2145	30000
3,5-Dimethoxyacetophenone in hexane	Bend 3530-3490	40-60	3120	8000	2590	20000	2155	30000
3-Methoxyacetophenone in alcohol	–	–	3085	3500	2490	7000	2185	16600
3,5-Dimethoxyacetophenone in alcohol	–	–	3180	5000	2630	10000	2185	26600
3,5-Dihydroxyacetophenone in alcohol	–	–	3210	50000	2650	10000	2180	25000

Comparison of the curves for 3,5-dimethoxy- and 3-methoxyacetophenone in alcohol indicates that the introducing of a second methoxy group at the meta position to the $COCH_3$ group gives rise to the same changes in absorption as the introduction of the second OH group at the same position in 3-hydroxyacetophenone. The curve consists of the same three bands in 3,5-dimethoxyacetophenone as in 3-methoxyacetophenone, their positions merely being shifted somewhat; in 3,5-dimethoxyacetophenone, the first two bands – the α_2''- and the α_1 bands – are shifted toward the longer wavelengths, viz.: the longwave edge of the α_2''-band by 140 A at $\varepsilon = 100$, and by 150 A at $\varepsilon = 1000$; the longwave edge of the α_1-band by 230 A at $\varepsilon = 2000$, etc. The maxima of these bands are shifted toward the longer wavelengths by 95 and 140 A, respectively, i.e., by nearly the same amount as in 3,5-dihydroxyacetophenone, compared to 3-hydroxyacetophenone (100 and 125 A, respectively). In both cases, the third α_1'-band, in contrast to the α_2''- and α_1-bands is located at the same λ as in the original compound. The similarity between the effect of the methoxy group in the 5 position and the effect of the hydroxyl group in the same position is also demonstrated by the fact that 3,5-dimethoxyacetophenone also exhibits an appreciable increase in intensity over 3-methoxyacetophenone (by the same amount as in 3,5-dihydroxyacetophenone, compared to the 3-hydroxy compound, namely, a fourfold increase) in the region of the minimum between the α_2''- and α_1-bands, which testifies to the increased absorption in the region of the acetophenone φ-band.

There are some differences, however, between the effects of the methoxy and hydroxy groups, viz.: a) the intensity of all three bands is perceptibly higher in 3,5-dimethoxyacetophenone over 3-methoxyacetophenone (40% in the α_2''- and α_1 bands, and 60% in the α_1'-band), whereas the band intensity in 3,5-dihydroxyacetophenone is the same as that in 3-hydroxyacetophenone; and b) 3,5-dimethoxyacetophenone does not exhibit the bend between 2960 and 2790 A that is found in 3,5-dihydroxyacetophenone.

The relationships between the absorption curves of 3,5-dimethoxyacetophenone and 3-methoxyacetophenone are the same in hexane (Fig. 2, Curves 2 and 3) as in alcohol, namely: the maxima of the α_2''- and α_1-bands are shifted toward the longer wavelengths in the former compound by about the same amount as in alcohol (95 and 130 A, respectively); the intensities of these bands increases 30 and 60%, respectively, in the former, as is the case in alcohol; the absorption intensity in the region of the minimum located between the α_2''- and α_1 bands in 3,5-dimethoxyacetophenone is more than 12 times as great as in 3-methoxyacetophenone. In contrast to what we observed in alcohol, the intensity of the α_1''-band does not change in hexane, while the longwave edge of the α_2''-band rises more steeply; the beginning of absorption (at $\varepsilon = 10$) of 3,5-dimethoxyacetophenone practically coincides with that of 3-methoxyacetophenone. In contrast to what occurs in alcohol, a bend exists between 3530 and 3490 A in 3,5-dimethoxyacetophenone in hexane, as was the case in 3-methoxyacetophenone, though not quite in so marked a form.

As we see in Fig. 2, as well as from the data in Table 2, the transition from the dihydroxy to the dimethoxy compound causes no appreciable change in the nature of the absorption. The band intensities do not change at all; the α_2'' and α_1 band maxima are shifted by a comparatively negligible amount toward the shorter wavelengths; and the longwave edges of the bands are shifted farther toward the shorter wavelengths in 3,5-dimethoxyacetophenone than in 3,5-dihydroxyacetophen. The longwave edge of the α_2''-band is shifted 180 A at $\varepsilon = 10$, and 110 A at $\varepsilon = 100$, the longwave edge of the α_1-band likewise being shifted 100 A at $\varepsilon = 2000$. Thus, the transition from 3,5-dihydroxyacetophenone to 3,5-dimethoxyacetophenone causes merely a slight shift of the maxima of the α_2''- and α_1-bands toward the shorter wavelengths, as we observed in the transition from 3-hydroxy to 3-methoxyacetophenone (by nearly the same amount in both cases), the shift of the band edges in that same direction being more pronounced. In contrast to our observations during the transition from 3-hydroxy- to 3-methoxyacetophenone, the transition from 3,5-dihydroxy- to 3,5-dimethoxyacetophenone involves, as we have pointed out above, the retention of the same absorption band intensity (the band intensity dropping perceptibly in the former transition [23]).

The presence of a bend on the curve for 3,5-dimethoxyacetophenone in hexane between 3530 and 3490 A, like the similar phenomenon in 3-methoxyacetophenone in hexane, is evidence of the complexity of the α_2-band in these compounds. This band apparently consists of two bands, one of them corresponding to the α_2-band of acetophenone; in both 3,5-dimethoxyacetophenone and 3-methoxyacetophenone the intensity of this band is the same as that in acetophenone itself, being merely shifted somewhat, it seems, toward the longer wavelengths in the former compound. In alcohol, this band, like the band in unsubstituted acetophenone, is shifted toward the shorter wavelengths, which explains its not appearing on the curves for alcoholic solutions.

3,5-Dihydroxyacetophenone in alcoholic solutions of sodium alcoholate. We investigated 3,5-dihydroxyacetophenone in alcoholic solutions of the alkali of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mol., with 100 mol. and 1000 mol. of sodium alcoholate. The concentrated solutions were an intense yellow, the color growing perceptibly fainter as they were diluted.

The absorption curve for the solution with 100 mols of sodium alcoholate (Table 5 and Fig. 3, Curve 2) starts at $\varepsilon = 100$ at $\lambda = 4550$ A, rising with a slight slope toward the shorter wavelengths to $\lambda = 4200$ A at $\varepsilon = 1000$.

When we pass from a solution with a concentration of 10^{-3} mol to one with 10^{-4} mol, we find an insignificant lack of coincidence of the beginning and end of absorption (totaling 100 A). The curve continues to rise, displaying a wide band with a maximum at $\lambda = 3660$ A and $\varepsilon = 5000$; it then drops down to a minimum at $\lambda = 3370$ A and $\varepsilon = 2000$, after which it gradually rises again, displaying a second band with a maximum at $\lambda = 2890$ A and $\varepsilon = 8000$. There is a third band in the shortwave region of the spectrum, with a maximum at $\lambda = 2350$ A and $\varepsilon = 26600$; the minimum between these latter two bands is located at $\lambda = 2660$ A and $\varepsilon = 2000$.

TABLE 5

3,5-Dihydroxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol. with 100 mols of sodium alcoholate			3,5-Dihdroxyacetophenone, 10^{-3} to $3 \cdot 10^{-5}$ mol. + 1000 mol. sodium alcoholate.		
λ		ε	λ		ε
4550		100	4550		100
4200		1000	3830		3500
4100		1000	3790	maximum	4000
3710		4000	3750		3500
3660	maximum	5000	3600		2500
3610		4000	3570	minimum	2000
3400		2500	3540		2500
3370	minimum	2000	3180		6000
3340		2500	3120	maximum	7000
2920		7000	3060		6000
2890	maximum	8000	2710		700
2860		7000	2695	minimum	600
2680		2500	2680		700
2660	minimum	2000	2350		23300
2640		2500	2345	maximum	26600
2360		23300	2340		23300
2350	maximum	26600	2290		16600
2340		23300			
2260		13300			

Increasing the number of molecules of acid to 1000 per molecule of the substance does not affect the character of the absorption curve; it has the same shape as when 100 mols of sodium alcoholate are present. The curve (Table 5 and Fig. 3, Curve 3) consists of the same three bands of about the same intensity, and the longwave end of the curve nearly coincides with that of the curve when 1000 mols of sodium alcoholate are present. Though the shape of the curve is the same, increasing the alkali concentration does produce several changes, namely: a) the maxima of the first α_2'-band and, even more so, of the second α_1-band, are shifted toward the longer wavelengths (130 and 230 A, respectively); the minimum between these two bands is likewise shifted toward the longer wavelengths by 200 A, though its intensity remains unchanged, a particularly large decrease in the absorption intensity as the alkali concentration is increased occurs in the region of the minimum lying between the last two bands (α_1- and α_1'), amounting to some 250%. Thus, the biggest changes in the absorption curve produced by the increase in the alkali concentration occur in the region of the α_1-band; this latter band is widened perceptibly. The superposition of its longwave edge on the α_2'-band results in a contraction of the latter, compared to the status when 100 molecules of sodium alcoholate are present.

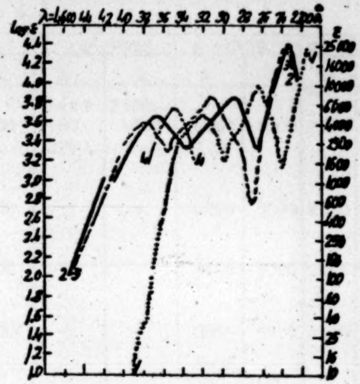


Fig. 3.

1) 3,5-Dihydroxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol., in alcohol; 2) 3,5-dihydroxyacetophenone, 10^{-3} - $3\cdot10^{-5}$ mol., in alcohol + 100 mols. C_2H_5ONa; 3) 3,5-dihydroxyacetophenone, 10^{-2} - $2\cdot10^{-5}$ mol., in alcohol + 1000 mols. C_2H_5ONa; 4) peak of the α_2-band of 3-hydroxyacetophenone in alcohol + 100 mols. C_2H_5ONa.

The data on the absorption band maxima of 3,5-dihydroxyacetophenone in alcohol and in alcoholic solutions containing 100 and 1000 mols. of sodium alcoholate are tabulated in Table 6. The corresponding data for 3-hydroxyacetophenone in alkali solutions [23] and for 3,5-dihydroxybenzaldehyde in alcohol and in alcoholic solutions of sodium alcoholate, according to N.A.Valyashko and M.M.Shcherbak [8], are also listed in this table.

Comparison of the absorption curves of 3,5-dihydroxyacetophenone in neutral alcohol and in an alcoholic solution containing 100 molecules of sodium alcoholate per molecule of the substance, as well as the data in Table 6, indicate that the presence of the alkali produces an appreciable and nearly parallel shift of all the absorption curves toward the longer wavelengths, viz.: at ε = 100, the longwave edge is shifted by 850 A, and at ε = 1000 by 670 A, the band maxima being shifted in the same direction by 450 A for α_2'', 240 A for α_1-, and 170 A for α_1'; both of the minima are also shifted toward the longer wavelengths, by 390 and 250 A, respectively. An increase in the concentration of the alkali causes a further shift, but only in the first two bands. The maximum of the α_2''-band is shifted another 130 A, and that of the α_1-band another 230 A, the presence of 1000 mols. of sodium alcoholate causing a certain decrease in the intensity of the α_2''-band and a further slight decrease of intensity in the α_1-band.

The foregoing observations, as we see in the data cited in Table 6, resemble what occurs in 3,5-dihydroxybenzaldehyde when various amounts of sodium alcoholate are present. Here again we observe a considerable shift of the whole absorption curve toward the longer wavelengths, by about the same amount as occurs in 3,5-dihydroxyacetophenone. The shift is 580 A for the α_2''-band, 470 A for the α_1-band, and 165 A for the α_1'-band for the latter compound with 1000 mols. of sodium alcoholate; this shift totals 510, 490, and 300 A, respectively, for 3,5-dihydroxybenzaldehyde when 2000 molecules of sodium alcoholate are present. Under the specified conditions, the maxima of the first two bands occupy almost the same positions in both of these compounds.

Comparison of the data for the absorption of 3,5-dihydroxyacetophenone in the presence of 100 and 1000 mols. of sodium alcoholate with the corresponding data for 3-hydroxyacetophenone (also see the curves in Fig. 3) shows that the shift of the curve toward the longer wavelengths is greater for the former compound for a given number of molecules of sodium alcoholate. This is particularly striking in the α_2''-band when 1000 mols. of sodium alcoholate are present; the position of the α_1'-band is practically the same in both instances. The effect of the alkali upon the two compounds is noticeably different in the region of

TABLE 6

Compounds	α_2"-band		φ-band		α_1-band		α_1'-band	
	λ	ε	λ	ε	λ	ε	λ	ε
3,5-Dihydroxyactophenone in alcohol	3210	5000	Bend 2960-2790	2500-4000	2650	10000	2180	25000
3,5-Dihydroxyacetophenone with 100 mols. of sodium alcoholate present............	3660	5000	–	–	2890	8000	2350	26600
3,5-Dihydroxyacetophenone with 1000 mols. of sodium alcoholate present............	3790	4000	–	–	3120	7000	2345	26600
3-Hydroxyacetophenone in alcohol with 100 mols. of sodium alcoholate present	3495	5000	–	–	2655	5000	2380	30000
3-Hydroxyacetophenone in alcohol with 1000 mols. of sodium alcoholate present............	3515	3500	–	–	Bend 2760-2560	3000-7000	2360	23300
3,5 Dihydroxybenzaldehyde in alcohol	3340	3500	–	–	2710	9000	2200	15000
3,5-Dihydroxybenzaldehyde with 20 mols. of sodium alcoholate present	3680	2500	–	–	2930	8000	2400	22000
3,5-Dihydroxybenzaldehyde with 2000 mols. of sodium alcoholate present	3850	4000	–	–	3200	8000	2500	20000

the α_1 band. When 100 mols. of sodium alcoholate are present, this band is shifted nearly twice as far toward the longer wavelengths in 3,5-dihydroxyacetophenone as it is in 3-hydroxyacetophenone; in the presence of 1000 molecules the band is not shifted at all in the latter compound, but diminishes in intensity and is manifested merely as a bend between 2760 and 2560 A. This situation is different with 3,5-dihydroxyacetophenone: increasing the alkali concentration results in a further, and more pronounced, shift of this band in the same direction. Moreover, though the absorption intensity is lowered considerably in the region of the minimum between the α_2"- and the α_1 bands when the amount of sodium alcoholate used with 3-hydroxyacetophenone is raised from 100 to 1000 mols., it is the absorption intensity in th region of the minimum between the α_1- and α_1' bands that is reduced in 3,5-dihydroxyacetophenone. The further shift of the curve for 3,5-dihydroxyacetophenone as the alkali concentration is increased indicates that the process of salt formation is not complete in this compound when 100 mols. of sodium alcoholate are present.

With complete salt formation in 3,5-dihydroxyacetophenone (when 1000 mols. of sodium alcoholate are present), the band shifts are, as we have pointed out, 580 A for the α_2"-band, 470 A for the α_1-band, and 165 A for the α_1'-band, from the curve in neutral alcohol; in 3-hydroxyacetophenone, these shifts are 400, 140, and 180 A, respectively. In other words, the presence of two salt-forming, symmetrical hydroxyl groups does not affect the amount of the shift of the α_1'-band, though it increases the shift of the α_2"-band some 50% and causes a particularly large shift of the α_1-band.

It must also be pointed out that the minima of the 3,5-dihydroxyacetophenone curve in alkaline solutions are located at approximately the same λ as the maxima of the 3-hydroxyacetophenone curve in solutions of equivalent concentration. Thus, in the presence of 100 mols. of sodium alcoholate, the maxima of the α_2"- and α_1-bands of 3-hydroxyacetophenone are located at 3495 and 2655 A, whereas the minima of 3,5-dihydroxyacetophenone lie at 3370 and 2660 A; corresponding figures for the 3-hydroxy compound in 1000 mols. of sodium alcoholate are 3515 and between 2760 and 2560 A, and for the 3,5-dihydroxy compound 3570 and 2675 A. This leads us to suppose that the slower rise of the longwave edge of the α_1 band in the latter compound and hence its perceptible widening are due to superposition in this absorption region, as is typical of 3-hydroxyacetophenone in a solution of the corresponding alkali concentration or in neutral alcohol.

In a solution containing 100 mols. of sodium alcoholate, the greater shift of the α_1-band in 3,5-dihydroxyacetophenone causes this band to lie approximately in the same region as the resorcin band in an excess of alkali, the maximum of which is located at λ = 2950 A and ε = 6000, according to N.A.Valyashko and M.M. Shcherbak [6].

3,5-Dimethoxyacetophenone in Alcoholic Solutions of Sodium Alcoholate

We investigated the absorption in the ultraviolet of 3,5-dimethoxyacetophenone in alcohol with 1000 mols. of sodium alcoholate, at solution concentrations of 10^{-3} and 10^{-4} mol.

The absorption curve starts at ε = 100 and λ = 3580 A and rises to a band maximum at λ = 3190 A and ε = 4000. After a fairly low minimum at λ = 2925 A and ε = 1000, the curve rises again, displaying a second band with a maximum at λ = 2620 and ε = 7000. The curve has one more minimum in the shortwave region, at λ = 2410 A and ε = 1000.

As we see from a comparison of the curves of 3,5-dimethoxyacetophenone in alcohol and in alcoholic solutions of sodium alcoholate (Fig. 4, Curves 1 and 2), as well as from the data in Table 7, the precence of the alkali does not affect absorption. The curve consists of the same three bands (the third band does not appear on the curve) as in neutral alcohol; the two curves nearly coincide in some areas. The presence of the alkali merely causes some drop in the intensity of the absorption bands as well as in the absorption in the region of the minimum between the α_2"- and α_1-bands; another effect of the alkali is to shift the minima somewhat toward the longer wavelengths (25 and 30 A, respectively).

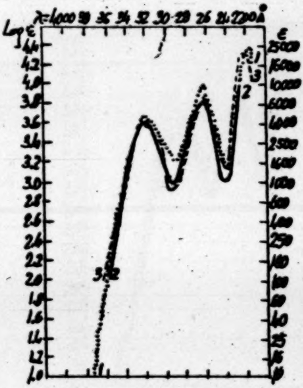


Fig. 4.

1) 3,5-Dimethoxyacetophenone, 10^{-2} - $3\cdot10^{-5}$ mol., in alcohol; 2) 3,5-dimethoxyacetophenone 10^{-3} - 10^{-4} mol., in alcohol + 1000 mols of C_2H_5ONa; 3) 3,5-dimethoxyacetophenone 10^{-3} - $3\cdot10^{-5}$ mol., in alcohol + 4000 mols. of HCl.

This effect of alkali upon the absorption of 3,5-dimethoxyacetophenone differs from its effect upon 3-methoxyacetophenone, in which the band maxima are shifted as follows: α_2" by 25 A toward the shorter wavelengths, and α_1 by 30 A toward the longer wavelengths (the shifts are the converse, as it happens, in 3,5-dimethoxyacetophenone and are smaller); moreover, the intensity of the minimum between the α_2" and α_1-bands does not change in 3-methoxyacetophenone, though the absorption intensity is less at the second minimum (exactly the opposite is the case with 3,5-dihydroxyacetophenone).

TABLE 7

Compound	α_2" Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
3,5-Dimethoxyacetophenone in alcohol ...	3180	5000	2630	10000	2185	26600
3,5-Dimethoxyacetophenone with 1000 mols. of sodium alcoholate present...	3190	4000	2620	7000	–	–

Comparison of the effect of alkali upon 3,5-dihydroxyacetophenone and upon 3,5-dimethoxyacetophenone indicates that the few changes in the absorption of 3,5-dihydroxyacetophenone when 1000 molecules of sodium alcoholate are present cannot be ascribed to salt formation, for they occur in 3,5-dimethoxyacetophenone as well. In fact, the extent of the drop in intensity of the α_2'- and α_1-bands is the same in both cases, the intensity of these bands being the same in these compounds in alkali as well.

3,5-Dihydroxy- and 3,5-Dimethoxyacetophenone in Alcoholic Solutions of Hydrogen Chloride

We investigated 3,5-dihydroxyacetophenone in alcoholic solutions of HCl of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mols. with 4000 molecules of HCl, and 10^{-4} mol with 40,000 molecules of HCl per molecule of the substance.

The absorption curve of the solution containing 4000 mols. of HCl (Fig. 5, Curve 2) consists of the same three bands as in the neutral alcohol solution, and is nearly parallel to the latter. As we see from the data in Table 8, the band maxima are located at nearly the same λ and ε. There is merely some decrease in the intensity of the α_2' and α_1 bands. There are also slight changes in the longwave edge of the α_2" band: it is shifted somewhat toward the shorter wavelengths (90 A at ε = 100 and 60 A at ε = 1000); the longwave edge of the α_1 band is likewise shifted toward the shorter wavelengths (100 A at ε = 2000). The minimum between the α_2" and α_1 bands is also shifted in that direction (by 45 A), the absorption intensity at this minimum being almost halved.

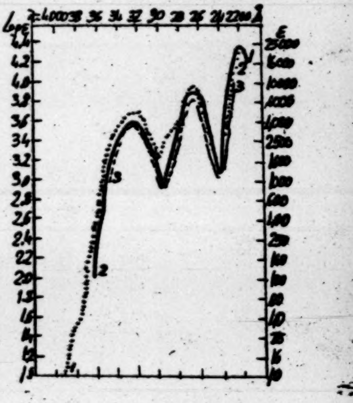


Fig. 5

1) 3,5-Dihydroxyacetophenone 10^{-2} - $2 \cdot 10^{-5}$ mol., in alcohol; 2) 3,5-dihydroxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol., in alcohol + 4000 mols. of HCl. 3) 3,5-dihydroxyacetophenone. 10^{-4} mol., in alcohol + 40000 mols. of HCl.

When HCl is present, the bend between 2960 and 2790 A, observed in neutral alcohol, is missing.

Nor does increasing the HCl concentration to 40000 molecules per molecule of 3,5-dihydroxyacetophenone cause any essential changes in the nature of the absorption. The absorption curve consists of the same α_2' and

TABLE 8

Compound	α_2'' Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
3,5-Dihydroxyacetophenone in alcohol .	3210	5000	2650	10000	2180	25000
3,5-Dihydroxyacetophenone with 4000 mols. of HCl..........................	3220	4000	2645	8000	2180	23300
3,5-Dihydroxyacetophenone with 40000 mols. of HCl..........................	3235	4000	2630	7000	–	–
3,5-Dimethoxyacetophenone in alcohol .	3180	5000	2630	10000	2185	26600
3,5-Dimethoxyacetophenone with 4000 mols. of HCl	3190	4000	2630	8000	2185	23300
3,5-Dimethoxyacetophenone with 40000 mols. of HCl..........................	3200	3500	2620	8000	–	–

α_1 bands (Fig. 5, Curve 3); moreover, the maxima of these bands are shifted only slightly. There is, apparently, a definite pattern in the nature of the band shifts due to HCl, namely: as the HCl concentration rises, the α_2'' band maximum is shifted increasingly, even though only slightly, toward the longer wavelengths (by 10 A with 4000 molecules of HCl present, and by 25 A when 40000 molecules of HCl are present); the maximum of the α_1 band, on the other hand, is shifted to the shorter wavelengths (by 5 A in the former case, and by 20 A, an amount that exceeds the margin of experimental error, in the second).

Some of the relationships noticed above are, no doubt, of a general nature, for they are also observed in 3-hydroxyacetophenone [23] and, as we shall see later, in 3,5-dimethoxyacetophenone as well. In 3-hydroxyacetophenone, the maximum of the α_2'' band is also shifted toward the longer wavelengths as the HCl concentration is increased (by 45 A when 40000 mols. of HCl are present), whereas the maximum of the α_1 band, on the other hand, is shifted toward the shorter wavelengths (by 10 A), the band intensities dropping to about the same degree as in 3,5-dihydroxyacetophenone.

3,5-Dimethoxyacetophenone was investigated in alcoholic solutions of HCl of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mol. with 4000 mol. of HCl, and 10^{-4} mol. with 40000 mol. of HCl. The absorption curves are shown in Fig. 4, while the data on the band maxima are tabulated in Table 8.

As we see from these figures, the presence of HCl does not affect the shape of the absorption curve in neutral alcohol, the curve consisting of the same bands. The slight changes in the curve are like those observed for 3,5-dihydroxyacetophenone; here again, the maximum of the α_2'' band is shifted somewhat toward the longer wavelengths, and, here again, the band intensity is somewhat lower, while the absorption at the minimum between the α_2'' and α_1 bands is diminished by the same amount as in 3,5-dihydroxyacetophenone. The difference between the two compounds insofar as the influence of HCl is concerned is that the long-wave edge of the α_2'' band is shifted toward the longer wavelengths (by 30 A at $\varepsilon = 100$) in 3,5-dimethoxyacetophenone, instead of toward the shorter wavelengths.

As in the case of 3,5-dihydroxyacetophenone, increasing the concentration of HCl to 40000 mols. per mol. of 3,5-dimethoxyacetophenone merely causes a further slight shift of the band maxima, that of the α_2'' band being shifted toward the longer wavelengths and that of the α_1 band toward the shorter ones. With these exceptions, the curve coincides with that recorded with 4000 mols. of HCl present.

3,5-Dihydroxyacetophenone in Concentrated and Dilute Sulfuric Acid

Like 3-hydroxyacetophenone, 3,5-dihydroxyacetophenone dissolves readily in concentrated sulfuric acid, the solution being colored an intense yellow. We investigated solutions with the following concentrations: 10^{-3}, 10^{-4}, and $4 \cdot 10^{-5}$ mol.

The absorption curve (Table 9 and Fig. 6, Curve 2) starts at $\varepsilon = 100$ and $\lambda = 4780$ A and rises gradually, with a marked slope toward the shorter wavelengths, to form a band with a maximum at $\lambda = 3730$ A and $\varepsilon = 4000$. After a comparatively shallow minimum, the curve rises again to a second wide and strong band with a maximum at $\lambda = 3035$ A and $\varepsilon = 13750$. The curve has a third band in the shortwave region, with a maximum at $\lambda = 2280$ A and $\varepsilon = 12500$. The minimum between the last two bands is located at $\lambda = 2600$ A and $\varepsilon = 1300$.

The figures on the absorption band maxima of 3,5-dihydroxyacetophenone in alcohol and in concentrated sulfuric acid are tabulated in Table 10. For the sake of comparison, the same table lists the figures for 3-hydroxyacetophenone under the same conditions and for 3,5-dihydroxyacetophenone in a 10% aqueous solution of sulfuric acid.

TABLE 9

3,5-Dihydroxyacetophenone, 10^{-3} - $4 \cdot 10^{-5}$ mol., in concentrated sulfuric acid.			3,5-Dihydroxyacetophenone, 10^{-4} - $4 \cdot 10^{-5}$ mol., in a 10% aqueous solution of sulfuric acid		
λ		ε	λ		ε
4780		100	3550		1000
4200		1000	3280		4000
3780		3500	3240	maximum	5000
3730	maximum	4000	3200		4000
3680		3500	3000		1600
3550		2000	2970	minimum	1300
3505	minimum	1600	2940		1600
3460		2000	2670		8000
3070		12500	2645	maximum	10000
3035	maximum	13750	2620		8000
3000		12500	2400		2500
2620		1600	2380	minimum	2000
2600	minimum	1300	2360		2500
2580		1600	2200		12500
2290		10000	2195	maximum	15000
2280	maximum	12500	2190		12500
2270		10000	2150		8750

TABLE 10

Compound	α_2' Band		α_2'' Band		φ -Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
3,5-Dihydroxyacetophenone in alcohol	–	–	3210	5000	Bend 2960-2970	2500-4000	2650	10000	2180	25000
3,5-Dihydroxyacetophenone in concentrated sulfuric acid	–	–	3730	4000	3035	13750	–	–	2280	12500
3,5-Dihydroxyacetophenone in a 10% aqueous solution of sulfuric acid...	–	–	3240	5000	–	–	2645	10000	2195	15000
3-Hydroxyacetophenone in concentrated sulfuric acid..................	4300	400	3720	5000	2935	13000	–	–	2270	10000

As we see from the data in Table 10, as well as from an inspection of the absorption curves for 3,5-dihydroxyacetophenone in alcohol and in concentrated sulfuric acid (Fig. 6), the latter produces fundmaental changes in absorption, namely:

a) Instead of the α_2'' band with a maximum at $\lambda = 3210$ A in neutral alcohol, we get a band with almost the same intensity but with a maximum at $\lambda = 3730$ A. This latter must be regarded as the same α_2'' band, but considerably shifted by the sulfuric acid nearly parallel, in the direction of the longer wavelengths. Compared to its position in alcohol, the long-wave edge of this band is shifted 1080 A at $\varepsilon = 100$, and 670 A at $\varepsilon = 1000$.

b) The α_1' band is apparently also shifted toward the longer wavelengths, but not nearly as much as the α_2'' band (its maximum being shifted only 100 A as against the 520 A for the α_2'' band). In contrast to the α_2'' band, its intensity is greatly reduced (halved) when the acid is present.

c) The α_1 band of 3,5-dihydroxyacetophenone in alcohol is missing when concentrated sulfuric acid is present, its place being taken by a deep minimum at $\lambda = 2600$ A on the curve in the acid.

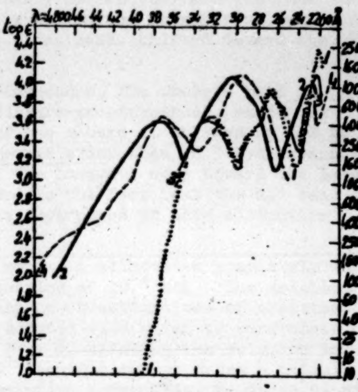


Fig. 6.

1) 3,5-Dihydroxyacetophenone, $10^{-2} - 2 \cdot 10^{-5}$ mol., in alcohol; 2) 3,5-dihydroxyacetophenone, $10^{-3} - 4 \cdot 10^{-5}$ mol., in concentrated H_2SO_4; 3) 3,5-dihydroxyacetophenone, $10^{-4} - 4 \cdot 10^{-5}$ mol., in 10% H_2SO_4; 4) 3-hydroxyacetophenone, $10^{-3} - 10^{-4}$ mol., in concentrated H_2SO_4

d) Absorption is sharply increased in the area of the bend in the curve in alcohol, lying between 2960 and 2790 A. The extremely strong band, with a maximum at $\lambda = 3035$ A that emerges resembles the φ band of 3-hydroxyacetophenone (with a maximum at $\lambda = 2935$ A, and unsubstituted acetophenone (max. at $\lambda = 2950$ A [27]) in concentrated sulfuric acid. As has been indicated previously [23], this band cannot be regarded as the α_1 band in alcoholic solution shifted toward the longer wavelengths and increased somewhat in intensity. The foregoing authors have shown that as the sulfuric acid concentration is increased, the α_1 band gradually grows weaker in unsubstituted acetophenone and shifts somewhat toward the longer wavelengths, thus entering the region of the φ band, which grows very much stronger at the same time. The absorption intensity also increases sharply in 3,5-dihydroxyacetophenone in the φ band when the concentrated acid is present (in alcohol, this band is manifested only as a bend in the curve), so that an extremely strong band is formed, as in 3-hydroxyacetophenone. The α_1 band that is shifted toward the longer wavelengths also falls into the region of this band, accounting for the perceptible widening of the φ band.

These features of the effect of H_2SO_4 upon the absorption of 3,5-dihydroxy acetophenone resemble those observed in 3-hydroxyacetophenone [23]. In the latter the curve is sharply shifted toward the longer wavelengths in concentrated sulfuric acid as against the curve in the alcohol solution; as we have pointed out, a φ band of the same intensity as in 3,5-dihydroxyacetophenone appears, the α_1 band vanishes, the maximum of the α_2'' band, which is shifted toward the longer wavelengths, occupies the same position as in 3,5-dihydroxyacetophenone, etc. The presence of a second OH group at the 5 position does give rise to some changes in the effect of the sulfuric acid, however. These changes are: a) the bend at $\lambda = {=}\sim 4300$ A exhibited on the 3-hydroxyacetophenone curve is not manifested on the

3,5-dihydroxyacetophenone curve. This is obviously due to the fact that the longwave edge of the α_2'' band is shifted perceptibly toward the longer wavelengths in the latter compound, with the α_2 band, on the other hand, shifted toward the shorter wavelengths.

b) Compared to the curve for 3-hydroxyacetophenone, the whole φ band is shifted toward the longer wavelengths in 3,5-dihydroxyacetophenone, as is the longwave edge of the α_1' band. The maximum of the φ band is shifted by 100 A; in 3,5-dihydroxyacetophenone, this band is somewhat wider than in 3-hydroxyacetophenone, largely because of a greater shift of the longwave edge toward the longer wavelengths. The latter circumstance may be due to the fact that the α_2'' band of 3,5-dihydroxyacetophenone in neutral alcohol is superposed in this absorption region.

The influence of sulfuric acid set forth above is eliminated completely when the 10^{-3} mol. solution is diluted to a concentration of 10^{-4} mol. The solution turns completely colorless. We made spectrographic investigations of solutions of 3,5-dihydroxyacetophenone in sulfuric acid diluted with water at concentrations of 10^{-4} and $4 \cdot 10^{-5}$ mol (Table 9). As we see in Fig. 6, diluting the solution in concentrated sulfuric acid with water from 10^{-3} to 10^{-4} mol produces a notable break in absorption (totaling 650 A). The absorption curve (Fig. 6, Curve 3) no longer has the φ band, present in the concentrated acid, all the three bands characteristic of 3,5-dihydroxyacetophenone in neutral alcohol or in alcohol with an excess of HCl present being restored completely. Moreover, comparison of the data on the band maxima of this compound in dilute sulfuric acid and in alcoholic solutions of HCl (Tables 8 and 10) indicates that they are located at nearly the same λ and ε in both cases. In other words, dilute sulfuric acid, like HCl, exerts negligible influence upon the absorption spectrum of 3,5-dihydroxyacetophenone, causing merely a slight shift of the α_2'' band maximum toward the longer wavelengths, (by 30 A) and of the minima, on the other hand, toward the shorter wavelengths, compared to the absorption curve in neutral alcohol. In contrast to the alcoholic solutions of HCl, the intensity of the α_1' band is reduced appreciably (halved) in the dilute sulfuric acid solution, its intensity remaining unchanged in the concentrated sulfuric acid.

3,5-Dimethoxyacetophenone in Concentrated and Water-Diluted Sulfuric Acid

Like 3-methoxyacetophenone, 3,5-dimethoxyacetophenone dissolves readily in concentrated sulfuric acid, the solution being an intense yellow. We investigated 10^{-3} and 10^{-4} mol. solutions spectrographically.

The absorption curve (Table 11 and Fig. 7, Curve 2) starts at $\varepsilon = 100$ and $\lambda = 4850$ A, rising with a noticeable slope toward the shorter wavelengths. The curve is rounded off considerably between 3950 and 3780 A and $\varepsilon = 1600$ and 2000, after which it rises more steeply, exhibiting a wide, strong band, with a maximum at $\lambda = 3150$ A and $\varepsilon = 10000$, equivalent to the φ band of 3,5-dihydroxyacetophenone in this same acid. After passing through a rather deep minimum at $\lambda = 2700$ A and $\varepsilon = 1000$, the curve rises again fairly steeply to another band with a maximum at $\lambda = 2300$ A and $\varepsilon = 13000$.

The data on the absorption band maxima for 3-methoxy- and 3,5-dimethoxyacetophenone in concentrated sulfuric acid are tabulated in Table 12; the table also lists the corresponding data for 3,5-dimethoxyacetophenone in neutral alcohol and in a dilute aqueous solution of sulfuric acid and for 3,5-dihydroxyacetophenone in concentrated sulfuric acid for the sake of comparison.

These figures, together with the curves for 3,5-dimethoxyacetophenone in alcohol and in concentrated sulfuric acid (Fig. 7, Curves 1 and 2) demonstrate that the spectrum produced in the acid is not the same as that in alcohol, viz.: a) the absorption curve is shifted quite pronouncedly toward the longer wavelengths, the start of absorption being shifted 1260 A at ε = 100; b) the α_1 band in alcohol, with a maximum at 2630 A, is missing, its place being taken in conc. H_2SO_4 by a deep minimum at λ = 2700 A; apparently, this band is also greatly shifted toward the longer wavelengths in the presence of the acid, but it is not evident owing to its falling within the region of a new band emerging in sulfuric acid, with a maximum at λ = 3150 A; c) the α_2'' band, present in alcohol, with a maximum at λ = 3180 A, is also missing. The point of inflection at 3780 A may represent this band, shifted appreciably toward the longer wavelengths and diminished in intensity; d) the α_1' band is likewise shifted toward the longer wavelengths in the acid (the maximum being shifted by 115 A), its intensity dropping appreciably (more than half).

TABLE 11

3,5-Dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in concentrated sulfuric acid			3,5-Dimethoxyacetophenone, 10^{-4} mol., in a 10% aqueous solution of sulfuric acid.		
λ		ε	λ		ε
4860		100	3400		1000
3950		1600	3210		4000
3780	band spread	2000	3180	maximum	5000
3710		2500	3150		4000
3200		8000	2940		2000
3150	maximum	10000	2925	minimum	1600
3100		8000	2910		2000
2750		1300	2670		8000
2700	minimum	1000	2650	maximum	10000
2650		1300	2630		8000
2320		10000	2400		2500
2300	maximum	13000	2385	minimum	2000
2280		10000	2370		2500
2220		8000	2260		10000

These changes in the absorption curve due to the presence of the acid resemble those observed in 3,5-dihydroxyacetophenone (see above), the curve of which was likewise shifted sharply toward the longer wavelengths, with the α_1 band missing, a strong φ band appearing, and so forth. In 3,5-dimethoxyacetophenone the α_1' band, like the other bands, is shifted toward the longer wavelengths somewhat more than in 3,5-dihydroxyacetophenone. The shift of the φ band is particularly

TABLE 12

Compound	α_2' Band		α_2'' Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
3-Methoxyacetophenone in concentrated sulfuric acid	~4200	~7000	3725	3000	2975	13000	–	–	2270	9000
3,5-Dimethoxyacetophenone in concentrated sulfuric acid	–	–	Bend 2950-3780	1600-2000	3150	10000	–	–	2300	13000
3,5-Dihydroxyacetophenone in concentrated sulfuric acid	–	–	3730	4000	3035	13750	–	–	2280	12500
3,5-Dimethoxyacetophenone in alcohol	–	–	3180	5000	–	–	2630	10000	2185	26600
3,5-Dimethoxyacetophenone in a 10% solution of sulfuric acid	–	–	3180	5000	–	–	2650	10000	–	–

striking, its longwave edge being superposed on the α_2'' band, accounting for the appearance of this band as merely a bend on the curve. Inasmuch as the shape of the absorption curve is the same in both of these compounds, it follows that the effect of sulfuric acid does not require the presence of a free OH group in the molecule; this influence is even somewhat greater (in the φ band region) in compounds containing a OCH_3 group. Hence, the relationships prevailing in the 3,5-dimethoxy and 3,5-dihydroxy compounds are the same as those observed in the 3-methoxy- and 3-hydroxyacetophenones. In the latter two, the absorption curves also have the same shape in concentrated sulfuric acid [23], the φ band being shifted somewhat more toward the longer wavelengths on the methoxy compound, while the α_2''-band is noticeably weaker.

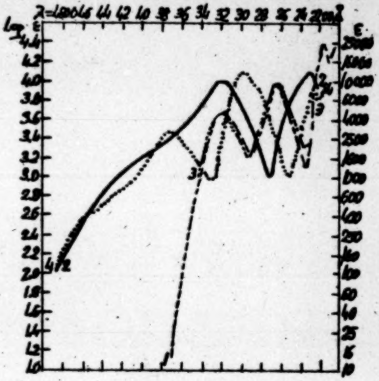


Fig. 7.

1) 3,5-Dimethoxyacetophenone, 10^{-2} - $3 \cdot 10^{-5}$ mol., in alcohol; 2) 3,5-dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in concentrated H_2SO_4; 3) 3,5-dimethoxyacetophenone, 10^{-4} mol., in 10% H_2SO_4; 4) 3-methoxyacetophenone, 10^{-3} - 10^{-4} mol., in concentrated H_2SO_4.

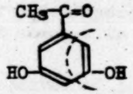
Comparison of the absorption curves of 3,5-dimethoxyacetophenone and 3-methoxyacetophenone (Fig. 7, Curves 1 and 4) reveals the same relationships as exist between 3,5-dihydroxy- and 3-hydroxyacetophenones, viz.: introducing a second methoxy group at the 5 position, like the introduction of a second OH group at that position, causes a further appreciable shift of the φ band toward the longer wavelengths, besides suppressing the bend at ~ 4200 A. The shift of the φ band is greater in the methoxy compound than in the hydroxy compound, (the maxima being shifted 175 and 100 A respectively). It follows that the effect of the number of meta methoxy groups, like that of the meta hydroxy groups, in concentrated sulfuric acid involves merely a greater development of the φ band, its widening and shifting towards the longer wavelengths, plus, apparently, some shift of the longwave edge of the α_1' band in the same direction.

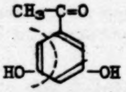
The effect of sulfuric acid established above vanishes completely when the 10^{-3} mol. solution is diluted with water to 10^{-4} mol., as was the case in 3,5-dihydroxyacetophenone and the other derivatives of acetophenone we investigated earlier [23]. The absorption curve (Table 11 and Fig. 7, Curve 3) of the solution with a concentration of 10^{-4} mol. starts at $\varepsilon = 1000$ and $\lambda = 3400$ A, not coinciding with the end of absorption of the 10^{-3} mol. solution in concentrated sulfuric acid. The curve consists of the same three bands as in the neutral alcohol solution (Table 12) and in the alcohol solution containing an excess of HCl.

Evaluation of the Absorption Spectra

It has been previously shown [6, 23] that introducing a hydroxyl group in the meta position to the carbonyl group in benzaldehyde or acetophenone develops a spectrum of the α-type, featuring increased absorption in the α_2 and α_1 bands. His spectrographic investigation of a series of dihydroxybenzaldehydes led N.A. Valyashko [28] to conclude that hydroxyl groups reinforce or weaken each other's action, depending upon their relative positions. Introducing a second OH group in the 4 position in 3-hydroxybenzaldehyde, for example, does not cause any shift of the α_2 band maximum; introducing the same group into 2-hydroxybenzaldehyde in the 3 or 5 position involves, on the other hand, a shift of this band toward the longer wavelengths. Investigation of the absorption spectrum of 3,5-dihydroxybenzaldehyde [6] and of 3,5-dihydroxyacetophenone indicates that the introduction of a second hydroxyl group into the 3-hydroxy compound at the 5 position likewise facilitates the further development of the α type spectrum, with the α_2 and α_1 bands shifted toward the longer wavelengths. At the same time, however, absorption is intensified perceptibly in the φ band, which is evidence of the simultaneous development of the φ state as well in the 3,5-dihydroxyacetophenone.

This effect of the second meta hydroxyl group may be explained as due to the nature of the conjugation of the OH and CO groups with the benzene ring and with each other. In 3,5-dihydroxyacetophenone, as in 3,5-dihydroxybenzaldehyde, the following two types of conjugation are possible:



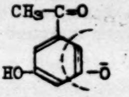


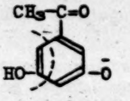
In both cases, the joint conjugation of these groups with the double bonds of the ring is paralled by the individual conjugation of an OH group with the benzene ring.

This is borne out by the absorption curve of 3,5-dimethoxyacetophenone. Inasmuch as the interactions of the OH and OCH_3 groups with the benzene ring are alike, we might expect the absorption curves of 3,5-dihydroxy- and 3,5-dimethoxyacetophenone to resemble each other, as is actually the case.

As in 3-hydroxyacetophenone, the presence of an excess of sodium alcoholate produces a marked shift of the absorption curve for 3,5-dihydroxyacetophenone toward the longer wavelengths. In contrast to the former, however, the absorption is greatly increased in the φ band as well as in the 3,5-dihydroxy compound. Whereas the α_1 band in the 3-hydroxy compound grows progressively weaker as it is shifted toward the longer wavelengths, in 3,5-dihydroxyacetophenone it is shifted even farther toward the longer wavelengths under these conditions, while retaining nearly the same intensity as in alcohol. This is apparently due to the greater absorption in the φ band. In other words, the α and φ states are strengthened in 3,5-dihydroxyacetophenone in alkaline solutions as well, thus accounting for the development of a spectrum of both the α and the φ type.

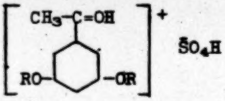
When 100 mols. of sodium alcoholate are present, only one of the hydroxyls participates in salt formation in some of the molecules, i.e., conjugations of the following type are possible in these molecules:





As a result, systems are conjugated together in which the carbonyl group is conjugated with the double bonds of the benzene ring conjointly with the OH group or with the $\bar{O}$ ion. This is responsible for the superposition, in the 3,5-dihydroxyacetophenone absorption curve when 100 mols. of sodium alcoholate are present, of the α_2'' band of 3-hydroxyacetophenone in the same medium, with a maximum at λ = 3495 A and ε = 5000 and of the α_2'' band of 3-hydroxyacetophenone in alcohol, with a maximum at λ = 3110 A and ε = 5000.

The absorption of 3-5-dihydroxyacetophenone, like that of 3,5-dimethoxyacetophenone, is subject to the same changes in concentrated sulfuric acid as those undergone by 3-hydroxy- and 3-methoxyacetophenone. Absorption is increased considerably in the bands that are typical of both the α and φ states. The reason for this must be sought in the formation of a salt with sulfuric acid of the following type:



as has been indicated earlier [23].

SUMMARY

1. The synthesis of 3,5-dihydroxyacetophenone from benzoic acid has been worked out, with certain changes in the methods of securing the individual intermediate products.

2. The absorption spectra of 3,5-dihydroxy- and 3,5-dimethoxyacetophenone have been investigated in hexane, alcohol, alcoholic solutions containing various amounts of sodium alcoholate and HCl, concentrated sulfuric acid, and sulfuric acid diluted with water.

3. It has been found that introducing a second OH group or a second OCH_3 group into 3-hydroxy- or 3-methoxyacetophenone at the 5 position promotes the increase of absorption in the bands that are typical of both the α and the φ states.

4. It has been found that the α_2 band of 3,5-dihydroxy- and 3,5-dimethoxyacetophenone is complex, as was the case in 3-methoxyacetophenone.

5. It has been shown that when an excess of sodium alcoholate is present, the absorption of 3,5-dihydroxyacetophenone is increased in the φ band as well as in the α_2 band.

6. Hydrogen chloride in alcoholic solutions and sulfuric acid in a dilute aqueous solution have no appreciable effect on the absorption spectra of the compounds in question. In these media the absorption curves differ but little from the curves of the respective compounds in neutral alcohol.

7. As in our observations of 3-hydroxy- and 3-methoxyacetophenone, 3,5-dihydroxy- and 3,5-dimethoxyacetophenone exhibit a marked increase in absorption in concentrated sulfuric acid, in both the α_2 and φ bands.

8. The singularities of the absorption spectra of 3,5-dihydroxy- and 3,5-dimethoxyacetophenone established above have been explained in the light of the possibility of their existing in two states: α and φ , which are in equilibrium and are characterized by the joint and individual conjugation of the groups with the double bonds of the benzene ring.

9. It has been shown that the α and φ states compete with each other in 3,5-dihydroxy- and 3,5-dimethoxyacetophenone, owing to the symmetrical arrangement of the OH or OCH_3 groups, which explains various peculiarities of their spectra, as compared with those of 3-hydroxy- and 3-methoxyacetophenone, respectively.

10. The fact that the α_2'' and α_1 bands in 3,5-dihydroxyacetophenone retain the same intensity as in 3-hydroxyacetophenone indicates that in the former compound only one of the hydroxyl groups at a time can participate in joint conjugation with the double bonds of the benzene ring.

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*See CB translation p. 1029 ff.

THE ABSORPTION SPECTRA AND STRUCTURES OF BENZENE DERIVATIVES

XVII. 2,6-DIHYDROXYACETOPHENONE AND ITS METHYL ESTERS

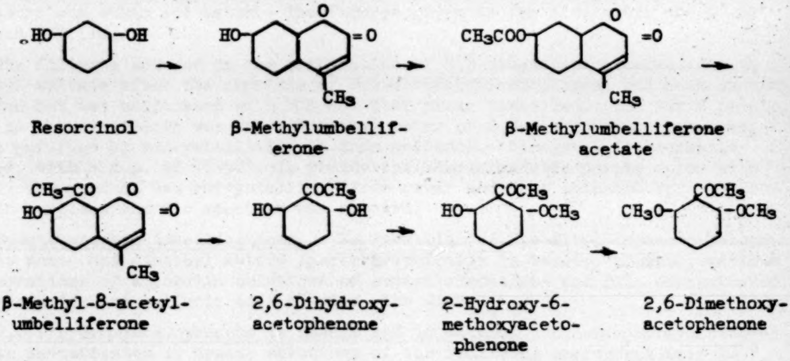
N. A. Valyashko and A. E. Lutsky

We have investigated symmetrical 3,5-dihydroxyacetophenone and its dimethyl ester previously [1]. We were also interested in making a spectrographic study of the corresponding symmetrical diortho substitutes of acetophenone, namely 2,6-dihydroxyacetophenone and its methyl esters, and in comparing their absorption curves with those of 3,5-dihydroxy- and 3,5-dimethoxyacetophenone, as well as with the absorption curves for 2,4-dihydroxyacetophenone and its esters, investigated by N.A.Valyashko and Yu.S.Rozum [2].

Synthesis of 2,6-dihydroxyacetophenone and its methyl ester. 2,6-Dihydroxyacetophenone was unknown for a long time, and it was only in 1934 that two methods for its synthesis were suggested almost simultaneously by Mauthner [3] and Limaye [4].

Mauthner started with metadinitrobenzene, converting it successively into 2-nitro-6-methoxybenzonitrile, 2,6-dimethoxybenzonitrile, 2,6-dimethoxyacetophenone, and 2,6-dihydroxyacetophenone. A Robertson [5] and Haller [6] synthesized a series of 2,6-dimethoxy- and 2,6-dihydroxy phenyl alkyl ketones by practically the same method.

Mauthner's method is not quite as simple as Limaye's, however, which we adopted. 2,6-Dihydroxyacetophenone and its mono and dimethyl esters were synthesized in the following series of transformations:


HO
OH
Resorcinol
O
HO
=O
CH₃
β-Methylumbelliferone
O
CH₃COO
=O
CH₃
β-Methylumbelliferone acetate
CH₃–CO
O
HO
=O
CH₃
β-Methyl-8-acetylumbelliferone
COCH₃
HO
OH
2,6-Dihydroxyacetophenone
COCH₃
HO
OCH₃
2-Hydroxy-6-methoxyacetophenone
COCH₃
CH₃O
OCH₃
2,6-Dimethoxyacetophenone

Of the available methods for preparing β-methylumbelliferone, the method due to Pechmann and Duisberg [7] must be considered the most efficient. This method involves the condensation of resorcinol with acetoacetic ester in the presence of concentrated sulfuric acid. The method has been worked up in detail by A. Pukirev [8], whose suggestions we have incorporated in the synthesis of this substance. The synthesized β-methylumbelliferone had a m.p. of 183-184° after recrystallization from alcohol; it readily reduced ammoniacal silver nitrate, and exhibited blue fluorescence with sulfuric acid and dilute alkali. The yield was 80%.

β-Methylumbelliferone acetate is ordinarily prepared by heating β-methylumbelliferone for 1-2 hours with acetic anhydride (Tiemann and Reimer [9], Baker [10], and others). We employed acetylation in the cold by the Chattaway method [11]. Acetylation we performed as follows: 88 g of β-methylumbelliferone was dissolved in an aqueous solution of alkali (23 g of NaOH); after adding crushed ice, we added a calculated quantity of acetic anhydride to the solution. The precipitated β-methylumbelliferone acetate was suction-filtered out, washed with water, and dried. Acetylation by this method is complete within 3 to 5 minutes, with a quantitative yield of a product of high purity (the product had the highest m.p. cited in the literature: 150°).

When β-methylumbelliferone acetate is heated with aluminum chloride, it undergoes a Fries rearrangement [12] – the acetyl group is shifted to the ortho position to the hydroxyl group. 40 g of pulverized, carefully desiccated β-methylumbelliferone acetate was heated with 4 to 5 times its weight of $AlCl_3$ from 20-150° during 70 to 80 minutes over an oil bath. After the reaction mass had cooled, it was treated with a concentrated solution of HCl. The solid mass of β-methyl-8-acetylumbelliferone was cleaved without purifying in order to secure 2,6-dihydroxyacetophenone.

A solution of 25 g of β-methyl-8-acetylumbelliferone in 10% NaOH was boiled gently over a sand bath for 60 to 70 minutes. After the reaction mass had cooled, it was acidulated with HCl. The precipitated 2,6-dihydroxyacetophenone was recrystallized from water and then consisted of light-straw crystals with a m.p. of 156-157°. They were recrystallized again for spectrographic purposes. The melting point of the pure product was 158°. The figure given in the literature is 157-158° [13,3].

2,6-Dimethoxyacetophenone was synthesized from 2,6-dihydroxyacetophenone by methylating it with dimethyl sulfate. The 2,6-dimethoxyacetophenone consisted of white crystals with a m.p. of 72-73° after repeated alternating recrystallization from petroleum ether and water. The figures given in the literature are 68-69° [14] and 73° [13].

The filtrate secured in the methylation of 2,6-dihydroxyacetophenone with dimethyl sulfate after the crystals of 2,6-dimethoxyacetophenone had been suction-filtered out was acidulated with HCl and then steam distilled. The solid precipitate in the distillate was the monomethyl ester of 2,6-dihydroxyacetophenone. It was purified by recrystallizing it from methanol. Elongated light-yellow needles, with a m.p. of 57-58°; it yields the characteristic purple color with $FeCl_3$. The product was recrystallized from water and from methanol for spectrographic purposes and its spectrum was checked.

Spectrographic investigations. We investigated 2,6-dihydroxyacetophenone and its mono- and dimethyl esters spectrographically in hexane, alcohol, various concentrations of alcoholic solutions of sodium alcoholate and HCl, concentrated sulfuric acid, and sulfuric acid diluted with water.

2,6-Dihydroxyacetophenone in hexane and in alcohol. 2,6-Dihydroxyacetophenone was investigated in hexane solutions of the following concentrations: 10^{-3},

10^{-4}, and $4 \cdot 10^{-5}$ mol. The absorption curve (Table 1, Fig. 1, Curve 2) starts at ε = 100 and λ = 4050 A and rises, forming a wide, intense band with a maximum at λ = 3420 A and ε = 7000. The rise is rather sloping from the start of the curve until λ = 3820 A, so that a slight bend at λ = 3820 A and ε = 500 is clearly evident at the longwave edge of this band. The shortwave edge of the band drops down to a minimum at λ = 2965 A and ε = 800, after which the curve rises again to form a narrower, very strong band with a maximum at λ = 2645 A and ε = 20000. There is still another band on the curve in the shortwave region, with a maximum at λ = 2265 A and ε = 15000; the minimum lying between the latter two bands is located at λ = 2410 A and ε = 1000.

TABLE 1

2,6-Dihydroxyacetophenone, 10^{-3} - $4 \cdot 10^{-5}$ mol., in hexane		2,6-Dihydroxyacetophenone, 10^{-2} - $6 \cdot 10^{-5}$ mol., in alcohol	
λ	ε	λ	ε
4050	100	4250	10
3820 bend	500	3810 bend	400
3500	6000	3480	4000
3420 maximum	7000	3425 maximum	5000
3340	6000	3370	4000
3020	1000	3010	800
2965 minimum	800	2990 minimum	700
2910	1000	2970	800
2670	17500	2720	11600
2645 maximum	20000	2690 maximum	13300
2620	17500	2660	11600
2430	1300	2480	1300
2410 minimum	1000	2435 minimum	1000
2390	12500	2390	1300
2265 maximum	15000	2290	10000
2250	12500	2275 maximum	13000
2230	10000	2260	10000
		2230	5000

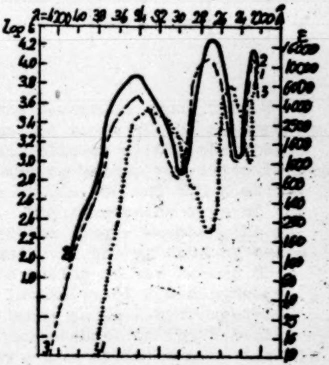


Fig. 1.

1) 2-Hydroxyacetophenone, 10^{-2} - 10^{-4} mol., in hexane; 2) 2,6-dihydroxyacetophenone, 10^{-3} - $4 \cdot 10^{-5}$ mol., in hexane; 3) 2,6-dihydroxyacetophenone, 10^{-2} - $6 \cdot 10^{-5}$ mol., in alcohol.

2,6-Dihydroxyacetophenone was investigated in alcohol solutions of the following concentrations: 10^{-2}, 10^{-3}, 10^{-4}, and $6 \cdot 10^{-5}$ mol. The 10^{-2} mol. solution was yellow. The absorption curve (Table 1; Fig. 1, Curve 3) starts at ε = 10 and λ = 4250 A and, rising, forms a broad band with a maximum at λ = 3425 A and ε = 5000. As in hexane, there is a clearly marked bend at the longwave edge of this band, at λ = 3810 A. The shortwave edge of the band drops down to a minimum at λ = 2990 A and ε = 700; then the curve rises again, forming a second, strong band, with a maximum at λ = 2690 A and ε = 13300. The shortwave edge of the latter band drops down to a minimum at λ = 2435 A and ε = 1000. There is another band in the shortwave region, with a maximum at λ = 2275 A and ε = 13000.

The data on the absorption band maxima of 2,6-dihydroxyacetophenone in hexane and in alcohol are listed in Table 2, together with the corresponding data for 2-hydroxyacetophenone, as found by N.A.Valyashko and Yu.S.Rozum [5].

As we see when we compare the absorption curves of 2,6-dihydroxyacetophenone and 2-hydroxyacetophenone (Fig. 1, Curves 1 and 2), the exhibit essentially the same absorption bands, denoted as the α_2'', α_1, and α_1' bands, as stipulated

TABLE 2

Compound	α_2' Band		α_2'' Band		φ - Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
2,6-Dihydroxyacetophenone in hexane	Bend 3820	500	3420	7000	–	–	2645	20000	2265	15000
2,6-Dihydroxyacetophenone in alcohol	Bend 3810	400	3425	5000	–	–	2690	13300	2275	13000
2-Hydroxyacetophenone in hexane	–	–	3250	3500	2900	600	2510	9000	over 2200	–
2-Hydroxyacetophenone in alcohol	–	–	3250	5000	–	–	2530	10000	–	–

earlier [16]. In other words, the introduction of the second OH group into 2-hydroxyacetophenone at the 6 position does not change the shape of the absorption curve. The only changes occuring in the curve are as follows: a) the absorption is shifted toward the longer wavelengths in the α_2'' and α_1 bands, viz.: the longwave edge of the α_2'' band is shifted 370 A in hexane at $\varepsilon = 100$ and 365 A at $\varepsilon = 10$ in alcohol, the band maximum being shifted 170 A. The same holds true of the α_1 band, the maximum of which is shifted 135 A toward the longer wavelengths in hexane and 160 A in alcohol; b) The absorption intensity of the α_2'' and α_1 bands in hexane is greatly increased (100% and more) by the adding of the second OH group in the ortho position, whereas the absorption intensity of 2,6-dihydroxyacetophenone in alcohol is nearly the same in these bands as in 2-hydroxyacetophenone; c) the φ band of 2-hydroxyacetophenone is not present in the 2,6-dihydroxyacetophenone curve. In this region the latter curve exhibits a noticeable rise in absorption intensity, as evidenced by the rise in the intensity of the minimum between the α_2'' and α_1 bands, together with its shift toward the longer wavelengths; d) The appearance of the α_1 band in 2-hydroxyacetophenone in the shortwave region, lying beyond 2200 A.

Comparison of the absorption curves of 2,6-dihydroxyacetophenone in hexane and in alcohol (Fig. 1, Curves 3 and 2) indicates that absorption is of the same character in both solvents. The band maxima are located at nearly the same λ and ε, with the exception of the α_1 band, whose maximum in alcohol is shifted 45 A toward the longer wavelengths from its position in hexane. The maxima of the α_2'' and α_1 bands grow perceptibly weaker, as we see in Table 2, without changing their locations, as in the case of the α_1 band. The longwave edge of the α_2'' band in alcohol is shifted slightly toward the shorter wavelengths, its shortwave edge, on the other hand, being shifted somewhat toward the longer wavelengths. This makes this band somewhat narrower in alcohol.

These relationships are somewhat like those observed in 2-hydroxyacetophenone [15], in which shifting from hexane to alcohol also caused no change in the position of the α_2'' band, merely shifting its longwave edge slightly toward the shorter wavelengths; here again, the maximum of the α_1 band is shifted slightly toward the longer wavelengths, though less so (by 20 A). In contrast to 2,6-dihydroxyacetophenone, when we turn to an alcoholic solution of 2-hydroxyacetophenone, we find the intensity of the absorption bands increasing rather than diminishing.

2-Hydroxy-6-methoxyacetophenone in hexane and in alcohol.. 2-Hydroxy-6-methoxyacetophenone was investigated in hexane solutions of the following concentrations: 10^{-3}, 10^{-4} and $2 \cdot 10^{-5}$ mol. The absorption curve (Table 3; Fig. 2, Curve 1) starts at ε = 100 and λ = 3810 A, and rises steeply, exhibiting a broad α_2'' band with a maximum at λ = 3345 A and ε = 7000. Then the curve drops to a minimum at λ = 2930 A and ε = 800 and rises again, exhibiting a very strong α_1 band with a maximum at λ = 2665 A and ε = 20000. Then the curve drops once more to a minimum at λ = 2385 A and ε = 1600 and, rising again, exhibits a third α_1' band with a maximum at λ = 2250 A and ε = 20000.

TABLE 3

2-Hydroxy-6-methoxy-acetophenone, 10^{-3} - $2\cdot10^{-5}$ mol., in hexane			2-Hydroxy-6-methoxy-acetophenone, 10^{-3} - $4\cdot10^{-5}$ mol., in alcohol		
λ		ε	λ		ε
3810		100	3880		100
3390		6000	3410		5000
3345	maximum	7000	3355	maximum	6000
3300		6000	3300		5000
2960		1000	3020		1300
2930	minimum	800	2985	minimum	1000
2900		1000	2950		1300
2680		17500	2745		12500
2665	maximum	20000	2705	maximum	15000
2650		17500	2670		12500
2400		2000	2400		1000
2385	minimum	1600	2380	minimum	800
2370		2000	2360		1000
2260		17500	2260		12500
2250	maximum	20000	2255	maximum	15000
2240		17500	2250		12500
2230		15000	2200		8000

We investigated alcoholic solutions of the following concentrations. 10^{-3}, 10^{-4}, and $4\cdot10^{-5}$ mol. The absorption curve (Table 3, Fig. 2, Curve 2) starts at ε = 100 and λ = 3880 A and rises steeply, exhibiting a α_2'' band with a maximum at ε = 6000 and λ = 3355 A. After a minimum at λ = 2985 A and ε = 1000, the curve exhibits an α_1 band with a maximum at λ = 2705 A and ε = 15000. It has a third, α_1' band in the shortwave region, with a maximum at λ = 2255 A and ε = 14000. The minimum between the latter two bands is located at λ = 2380 A and ε = 800.

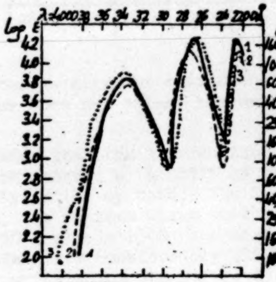


Fig. 2.

1) 2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $2\cdot10^{-5}$ mol., in hexane; 2) 2-hydroxy-6-methoxyacetophenone, 10^{-3} - $4\cdot10^{-5}$ mol., in alcohol, 3) 2,6-dihydroxyacetophenone, 10^{-3} - 4 10^{-5} mol., in hexane.

The data on the absorption band maxima of 2-hydroxy-6-methoxyacetophenone in hexane and in alcohol are listed in Table 4, together with data on 2,6-dihydroxyacetophenone and 2-hydroxy- and 2-methoxyacetophenone [15] for the sake of comparison.

As we see from Table 4 as well as from the curves reproduced in Fig. 2, the absorption of 2-hydroxy-6-methoxyacetophenone in alcohol is of the same nature as that in hexane. As in the case of 2,6-dihydroxyacetophenone, the maxima of the α_2'' and α_2' bands in alcohol are located at the same λ as in hexane; their intensity in alcohol is again somewhat lower than that in hexane. In 2-hydroxy-6-methoxyacetophenone the maximum of the α_1 band is also shifted toward the longer wavelengths in alcohol, and by the same amount as in the case of 2,6-dihydroxyacetophenone (by 40 A). In contrast to the latter the longwave edge of the α_2'' band of 2-hydroxy-6-methoxyacetophenone is shifted somewhat toward the longer wavelengths in alcohol (70 A at ε = 100), compared to the curve in hexane. This takes place only up to ε = 2500, however, where the alcohol curve intersects the hexane

TABLE 4

Compound	α_2' Band		α_2'' Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
2-Hydroxy-6-methoxyacetophenone in hexane	–	–	3345	7000	–	–	2665	20000	2250	20000
2-Hydroxy-6-methoxyacetophenone in alcohol	–	–	3355	6000	–	–	2705	15000	2255	15000
2,6-Dihydroxyacetophenone in hexane	Bend 3820	500	3420	7000	–	–	2645	20000	2265	15000
2-Hydroxyacetophenone in hexane	–	–	3250	3500	2900	600	2510	9000	–	–
2-Methoxyacetophenone in hexane....................	3200	250	2970	3500	2650	1000	2410	8000	–	–

curve. At $\varepsilon = 4000$ the alcohol curve is at shorter wavelengths than in hexane. Apparently, methylating one of the hydroxyl groups does not affect the nature of the compound's interaction with alcohol.

Comparison with 2-hydroxyacetophenone indicates that the introduction of the methoxy group into that compound at the 6 position causes: a) A shift of the absorption toward the longer wavelengths, especially in the α_1 band. The longwave edge of the α_2'' band is shifted 100 A at $\varepsilon = 100$, its maximum being shifted 95 A; the longwave edge of the α_1 band being shifted 250 A at $\varepsilon = 2500$, its maximum being shifted 155 A; b) The intensity of the bands rises considerably (100%); c) The φ-band of 2-hydroxyacetophenone is not manifested on the curve; d) The absorption rises sharply at the minimum between the α_2'' and α_1 bands (about fivefold); and e) An α_1' band appears in the shortwave region.

The above-mentioned effects of adding a methoxy group to 2-hydroxyacetophenone at the 6 position are the same as the effects of adding an OH group at the same position (vide supra). The difference is only quantitative, plus the fact that introducing the OCH_3 group causes a greater shift of the α_1 band, while adding the OH group causes a greater shift of the α_2'' band. It likewise follows that the effect of the methoxy group at the 6 position is not the same as the effect of that group at the 4 position. Introducing a OCH_3 group at the 4 position in 2-hydroxyacetophenone causes a shift of the α_2'' and α_1 bands toward the shorter wavelengths, as has been shown earlier [15], and increases absorption appreciably in the φ-band with a maximum at $\lambda = 2735$ A.

Compared to 2-methoxyacetophenone, 2-hydroxy-6-methoxyacetophenone exhibits a sharp shift of the whole absorption curve toward the longer wavelengths (the band maxima being shifted as follows: α_2'' by 375 A, α_1 by 255 A), their intensity also rising appreciably (100 to 150%).

The curve for 2,6-dihydroxyacetophenone in hexane is reproduced in Fig. 2 (Curve 3). Comparison of this curve with that for 2-hydroxy-6-methoxyacetophenone shows that methylation of one of theortho hydroxyl groups causes no essential change in the absorption curve, only slight changes in the positions of the band maxima taking place: the α_2'' band is shifted somewhat toward the shorter wavelengths, its longwave edge being shifted 240 A at $\varepsilon = 100$ and 100 A at $\varepsilon = 1000$, while its maximum is shifted 75 A. The maximum of the α_1' band is also shifted toward the shorter wavelengths; on the other hand, the α_1 band is shifted somewhat toward the longer wavelengths (by 20 A). The band intensities either remain the same (as in the α_2'' and α_1 bands) when one of the hydroxyl groups is methylated or increase somewhat (as in the α_1' band).

These relationships differ from those observed in the transition from

2-hydroxyacetophenone to 2-methoxyacetophenone. In this latter case [15] the whole absorption curve is markedly shifted toward the shorter wavelengths (the maximum of the α_2'' band by 280 A, and that of the α_1 band by 100 A), though the intensity of these bands remains the same as in the original hydroxy compound, as is the case in 2-hydroxy-6-methoxyacetophenone.

2,6-Dimethoxyacetophenone in hexane and in alcohol. We investigated 2,6-dimethoxyacetophenone in hexane solutions of the following concentrations: 10^{-2}, 10^{-3}, and 10^{-4} mol.

The absorption curve (Table 5; Fig. 3, Curve 2) starts at $\varepsilon = 10$ and $\lambda = 3200$ A and rises rather steeply, exhibiting a narrow band with a maximum at $\lambda = 2775$ A and $\varepsilon = 5000$. There is a bend between 3090 and 3020 A and $\varepsilon = 250 - 500$ on the longwave side of this band. A rather shallow minimum at $\lambda = 2665$ A and $\varepsilon = 1600$ is followed by a second band with a maximum at $\lambda = 2510$ A and $\varepsilon = 6000$. Then the curve drops down to a minimum at $\lambda = 2410$ A and $\varepsilon = 3000$ and, rising again, breaks off at $\lambda = 2230$ A and $\varepsilon = 10000$.

TABLE 5

2,6-Dimethoxyacetophenone, 10^{-2} - 10^{-4} mol, in hexane			2,6-Dimethoxyacetophenone, 10^{-3} - 10^{-4} mol, in alcohol		
λ		ε	λ		ε
3200		10	3340		100
3100		160	2840		3500
3020	bend	500	2810	maximum	4000
2800		4000	2780		3500
2775	maximum	5000	2700		1600
2750		4000	2675	minimum	1300
2690		2000	2650		1600
2665	minimum	1600	2570		3500
2640		2000	2555	maximum	4000
2520		5000	2540		3500
2510	maximum	6000	2420		1000
2500		5000	2400	minimum	800
2430		3500	2380		1000
2410	minimum	3000	2200		10000
2390		3500			
2230		10000			

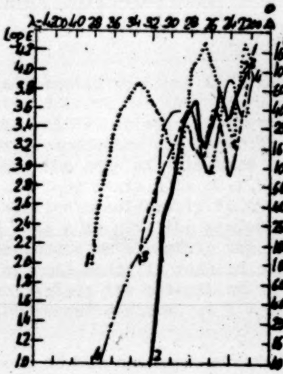


Fig. 3.

1) 2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $2 \cdot 10^{-5}$ mol., in hexane; 2) 2,6-dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in hexane; 3) 2,6-dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol; 4) 2-methoxyacetophenone, 10^{-3} - 10^{-4} mol., in hexane.

2,6-Dimethoxyacetophenone was investigated in alcohol solutions of the following concentrations: 10^{-3} and 10^{-4} mol. The curve (Table 5; Fig. 3, Curve 3) consists of the same two bends as in hexane. The curve starts at $\lambda = 3340$ A, rising steeply at first and then more slowly. The band maxima are located at $\lambda = 2810$ A and $\varepsilon = 4000$ and $\lambda = 2555$ A and $\varepsilon = 4000$, respectively; the minima are located at $\lambda = 2675$ A and $\varepsilon = 1300$ and at $\lambda = 2400$ A and $\varepsilon = 800$.

The data on the absorption band maxima of 2,6-dimethoxyacetophenone in hexane and in alcohol are listed in Table 6. The same table lists, for the sake of comparison, the corresponding data for 2-hydroxy-6-methoxyacetophenone, 2,6-dihydroxyacetophenone, and 2-methoxyacetophenone in hexane, as given by N.A.Valyashko and Yu.S.Rozum [15].

TABLE 6

Compound	α_2" Band		φ-Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
2,6-Dihydroxyacetophenone in hexane	3420	7000	–	–	2645	20000	2265	15000
2-Hydroxy-6-methoxyacetophenone in hexane.........	3345	7000	–	–	2665	20000	2250	20000
2,6-Dimethoxyacetophenone in hexane	Bend 3090-3020	250-500	2775	5000	2510	6000	–	–
2,6-Dimethoxyacetophenone in alcohol	–	–	2810	4000	2555	4000	–	–
2-Methoxyacetophenone in hexane	2970-3250	3500-250	2650	1000	2410	8000	–	–

Comparison of the absorption curves of 2,6-dimethoxyacetophenone in hexane and in alcohol indicates that the curve in the latter solvent has the same shape as in the former one. All that occurs are some band shifts, to wit: in alcohol, the band located within the region of the φ band of acetophenone and other benzene derivatives is shifted toward the longer wavelengths; the edge of this band is shifted especially far (230 A at $\varepsilon = 1000$), while the band maximum is shifted 35 A; the shortwave edge of the second, α_1, band is also shifted considerably in that direction, whereas its longwave edge remains fixed. As a result, the maximum of this band is shifted somewhat in alcohol toward the longer wavelengths, the band itself being perceptibly narrowed. The intensity of both bands is reduced somewhat in alcohol (by factors of 1.5 and 1.25, respectively); the absorption intensity is also greatly diminished in alcohol at the second minimum, at $\lambda = 2400$ A (by a factor of 3.5).

As we have established above, methylation of one of the hydroxyl groups in 2,6-dihydroxyacetophenone causes no essential changes in the absorption curve, except for a comparatively slight shift of the α_2" band toward the shorter wavelengths and of the α_1 band toward the longer ones. The situation is different when we pass from 2-hydroxy-6-methoxyacetophenone to 2,6-dimethoxyacetophenone, i.e., when both of the hydroxyl groups are methylated, as is shown by a comparison of the curves and of the data in Table 6. The nature of absorption now changes, viz.: a) absorption is shifted markedly toward the shorter wavelengths. At $\varepsilon = 100$ in hexane, the longwave edge of the absorption curve of 2,6-dimethoxyacetophenone is shifted 720 A compared to the 2-hydroxy-6-methoxyacetophenone curve, the shift being 710A at $\varepsilon = 1000$. The absorption of 2,6-dimethoxyacetophenone is sharply diminished in the region of the α_2' band of 2,6-dihydroxyacetophenone and 2-hydroxy-6-methoxyacetophenone, being manifested in hexane merely as a bend between 3090 and 3020 A. This bend lies in the same absorption region as the α_2' band of unsubstituted acetophenone or 2,6-dimethoxyacetophenone. b) The first band of 2,6-dimethoxyacetophenone lies in the same absorption region as the φ-band of acetophenone, phenol, and other compounds. In acetophenone, this band is located at the same λ (at $\lambda = 2770$ A and $\varepsilon = 1000$ [17]), as in 2,6-dimethoxyacetophenone, though the band is five times as strong in this band region in the latter compound. c) Fundamental changes also occur in the α_1 band region: its maximum is shifted 155 A toward the shorter wavelengths, compared to 2-hydroxy-6-methoxyacetophenone, and its intensity is diminished by a factor of 3.5. Owing to the increase in the intensity of absorption at the minimum at λ = 2410 A by nearly 100% as against the level in 2-hydroxy-6-methoxyacetophenone, this band is manifested merely as a narrow little band. The whole absorption curve resembles that of the dimethyl ester of resorcinol.

All the changes in the curves observed when we make the transition from 2,6-dihydroxyacetophenone or 2-hydroxy-6-methoxyacetophenone to 2,6-dimethoxyacetophenone in hexane are also found to exist in the curves recorded in alcohol. These changes are, apparently, typical of the foregoing ortho derivatives, for they are not present in the previously investigated 3-hydroxy- [18] and 3,5-dihydroxyacetophenone [1], methylation of which caused merely slight changes in the band positions. Moreover, they are somewhat like the changes observed in the curve of 2-hydroxyacetophenone when the latter is methylated (cf Table 4).

Comparison with the curve of 2-methoxyacetophenone in hexane (Fig. 3, Curve 4) shows that the introduction of a second OCH_3 group at the ortho position to the carbonyl group results in a perceptible change in absorption. The start of absorption, at ε = 10, is shifted about 400 A toward the shorter wavelengths, and the α_2'' band of 2-methoxyacetophenone, with a maximum at λ = 2970 A, is not present in 2,6-dimethoxyacetophenone. It may be shifted toward the shorter wavelengths; this would explain the appreciable increase in absorption intensity in the region of the φ band of 2-methoxyacetophenone. The α_1 band of 2,6-dimethoxyacetophenone, on the other hand, is shifted toward the longer wavelengths, compared to 2-methoxyacetophenone (the maximum being shifted by 100 A), while its intensity drops off slightly. Thus, introducing a second OCH_3 group in the 6 position into 2-methoxyacetophenone produces a noticeable shift of absorption toward the shorter wavelengths, the longwave α_2'' band usually found on the curve of these carbonyl compounds being absent (or greatly diminished in intensity).

The behavior of 2,6-dimethoxyacetophenone described above is, it seems, peculiar to diortho-substituted compounds, i.e., a marked shift of absorption toward the shorter wavelengths is related to the presence of two methoxy groups in ortho positions. This absorption shift is absent, to be sure, when a second OCH_3 group is added to 2-methoxyacetophenone at the 4 position. To judge from the findings of N.A.Valyashko and Yu.S.Rozum [15], the absorption curve is hardly changed in that case: the longwave region of the 2,4-dimethoxyacetophenone curve practically coincides with that of 2-methoxyacetophenone, the maximum of the α_2'' band being shifted only 20 A toward the shorter wavelengths, and so forth. Nor is it present in 3,5-dimethoxyacetophenone, which has a very strong α_2' band with a maximum at λ = 3120 A. The absorption curve of 2,6-dimethoxyacetophenone lies much farther toward the shortwave end of the spectrum than does that of 3,5-dimethoxyacetophenone. This shift of absorption chiefly involves the longwave band, for there is relatively little difference between 2,6-dimethoxyacetophenone on the one hand, and 2,4-dimethoxyacetophenone and 3,5-dimethoxyacetophenone, on the other, as far as the absorption in the region of the α_1 band is concerned: this band maximum is located at λ = 2510 A and ε = 6000, 2580 A and ε = 12000, and 2590 A and ε = 20000, respectively, in hexane; its strength is much lower, however, in 2,6-dimethoxyacetophenone (by factors of 2 and 3.3, respectively). It should be noted that all these singularities are observed only in the methoxy compounds, and not in the hydroxy compounds.

2,6-Dihydroxyacetophenone in alcoholic solutions of sodium alcoholate. 2,6-Dihydroxyacetophenone was investigated in alkaline solutions of the following concentrations: 10^{-3} and 10^{-4} mol. with 2 molecules of sodium alcoholate per molecule of the substance, and 10^{-3} and 10^{-4} mol. with 100 molecules and 1000 molecules of sodium alcoholate per molecule of the substance. The alkaline solutions were a bright yellow, the color intensity growing fainter as the solutions were diluted.

When 2 molecules of sodium alcoholate are present, the absorption curve (Table 7; Fig. 4, Curve 2) starts at ε = 100 and λ = 4710 A, rises upward with a pronounced slope toward the shorter wavelengths, and ends at ε = 1000 and λ = 4380 A. Diluting the solution from 10^{-3} mol. to 10^{-4} mol. weakens its color considerably. The start of absorption in this solution does not coincide with the end of absorption in the 10^{-3} mol. solution, being shifted far toward the shorter wavelengths (500 A). The absorption curve almost coincides with that of 2,6-dihydroxyacetophenone in neutral alcohol (Fig. 4 and the data in Table 8). The only difference between the two curves as far as the bands are concerned is the comparatively slight shift of the α_2" and α_1' bands toward the shorter wavelengths and of the α_1 band toward the longer wavelengths. The change in the region of the minimum between the α_2" and α_1 bands is more significant. It is shifted 230 A toward the longer wavelengths in the 10^{-3} mol. solution and nearly vanishes in the 10^{-4} mol. solution. The coincidence of the curves for 2,6-dihydroxyacetophenone in neutral alcohol and in a 10^{-4} mol. alcohol solution containing 2 molecules of sodium alcoholate indicates that the sodium salt formed in the 10^{-3} mol. solution undergoes nearly complete alcoholysis when the solution is diluted to a concentration of 10^{-4} mol, thus restoring the absorption spectrum of the neutral alcohol solution.

TABLE 7

2,6-Dihydroxyacetophenone, 10^{-3} - 10^{-4} mol, in alcohol + 2 molecules of sodium alcoholate			2,6-Dihydroxyacetophenone, 10^{-3} - 10^{-4} mol, in alcohol + 100 molecules of sodium alcoholate		
λ		ε	λ		ε
4710		100	4800		100
4380		1000	3970		6000
3790		1000	3860	maximum	7000
3480		5000	3750		6000
3420	maximum	6000	3300		700
3360		5000	3230	minimum	600
3250		600	3160		700
3220	minimum	500	2920		8000
3190		600	2865	maximum	10000
3130		11000	2810		8000
3020		1000	2630		1300
2780		10000	2605	minimum	1000
2710	maximum	13000	2580		1300
2640		10000	2450		11000
2440		1600	2415	maximum	13000
2420	minimum	1300	2380		10000
2400		1600	2260		5000
2270		10000	2240	minimum	4000
2250	maximum	13000	2220		5000
2230		10000	2170		10000
2150		3500			

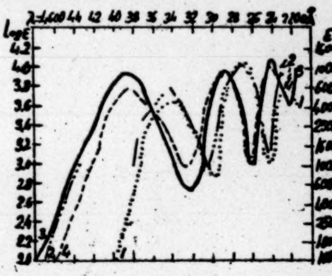


Fig. 4

1) 2,6-Dihydroxyacetophenone, 10^{-2} - $6 \cdot 10^{-5}$ mol., in alcohol; 2) 2,6-dihydroxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 2 molecules C_2H_5ONa; 3) 2,6-dihydroxyacetophenone 10^{-3} - 10^{-4} in alcohol + 10 molecules C_2H_5ONa; 4) 2,6-dihydroxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 1000 molecules C_2H_5ON

No alcoholysis occurs in the solution containing 100 molecules of sodium alcoholate per molecule of 2,6-dihydroxyacetophenone. The curve for the 10^{-3} mol. solution (Table 7; Fig. 4, Curve 3) coincides entirely with the curve for a solution of the same concentration containing 2 molecules of sodium alcoholate per molecule of the substance. This indicates that the same salt-formation effect is obtained in the latter case in concentrated solutions as with an excess of sodium alcoholate present. The curve continues to rise at a slant, without a break, exhibiting a broad band with a maximum at λ = 3860 A and ε = 7000. Then the curve drops down to a minimum at λ = 3230 A and ε = 600 and, rising again, forms a second band, with a maximum at λ = 2865 A and ε = 10000. There is still another band, with a maximum at λ = 2415 A and ε = 13000, in the shortwave region. The minimum between the latter two bands is located at λ = 2605 A and ε = 1000. The curve has a third minimum in the far ultraviolet, at λ = 2240 A and ε = 6000.

Increasing the number of molecules of sodium alcoholate to 1000 per molecule of the substance yields an absorption curve that differs but little from the curve produced with 100 molecules of sodium alcoholate present. The band maxima (Fig. 4, Curve 4) are located at the same λ and ε, within the limits of experimental error. When 1000 molecules of sodium alcoholate are present, we merely find a perceptible shift of the longwave edge of the first band toward the shorter wavelengths (by 200 A at ε = 100 and ε = 1000), plus an increase in absorption intensity at all the minima, especially the first one (nearly 100%).

The data on the absorption band maxima of 2,6-dihydroxyacetophenone in alcohol and in alcoholic solutions containing various amounts of sodium alcoholate are listed in Table 8. The table also gives the data for 2-hydroxyacetophenone [15] and 3,5-dihydroxyacetophenone [1] when 1000 molecules of sodium alcoholate are present per molecule of the substance.

TABLE 8

Compound	α_2'' Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
2,6-Dihydroxyacetophenone in alcohol.	3425	5000	2690	13300	2275	13000
2,6-Dihydroxyacetophenone in alcohol + 2 molecules of sodium alcoholate.	3420	6000	2710	13000	2250	13000
2,6-Dihydroxyacetophenone in alcohol + 100 molecules of sodium alcoholate	3860	7000	2865	10000	2415	13000
2,6-Dihydroxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	3855	6000	2875	10000	2415	13000
3,5-Dihydroxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	3515	3500	Bend 2760-2560	3000-7000	2360	23300
2-Hydroxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	3625	5370	Bend 3000	5000	–	–

Comparison of the absorption curve of 2,6-dihydroxyacetophenone in alcohol with the one in the presence of 1000 molecules of sodium alcoholate (Fig. 4, Curves 1 and 4) indicates that the formation of a salt causes a large shift of the whole absorption band toward the longer wavelengths. The bands of 2,6-dihydroxyacetophenone in the alkaline solution are the same as in alcohol, but they, i.e., the α_2', α_1, and α_1' bands, are all shifted in parallel toward the longer wavelengths. The α_2'' band undergoes a particularly large shift when alkali is present. The band intensities are practically unchanged in the alkaline solution: the intensity of the α_2'' band rises somewhat (20%) and that of the α_1 band is diminished (by a factor of 1.3). The minima are also shifted appreciably toward the longer wavelengths, the absorption intensity of these minima rising somewhat in the alkaline solution.

We see from Fig. 5, which gives the absorption curves of 2-hydroxy- and 2,6-dihydroxyacetophenone in alcoholic solutions containing 1000 molecules of sodium alcoholate, that 2,6-dihydroxyacetophenone features absorption in a longer wavelength region of the spectrum than 2-hydroxyacetophenone. In contrast to 2-hydroxyacetophenone, 2,6-dihydroxyacetophenone has a strong, sharply marked, α_1 band in an alkaline solution. The difference in the position of the α_2" band between 2-hydroxy- and 2,6-dihydroxyacetophenone in alkaline solutions, however, does not seem to be an indication of any quantitative difference in the action of the sodium alcoholate upon them. In fact, the difference in the positions of this band in alkali is found to be almost the same as in alcohol solutions of these compounds. At $\varepsilon = 100$, for example, the absorption of 2,6-dihydroxyacetophenone is shifted by exactly the same amount, compared to that of 2-hydroxyacetophenone, in neutral alcohol as in an alkaline solution, namely 330 A toward the longer wavelengths.

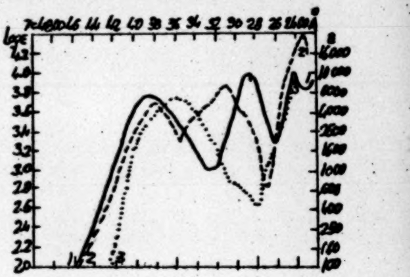


Fig. 5.

1) 2,6-Dihydroxyacetophenone, 10^{-3} -10^{-4} mol., in alcohol + 1000 molecules C_2H_5ONa;2) 3,5-dihydroxyacetophenone, 10^{-3} - $3\cdot10^{-5}$ mol., in alcohol + 1000 molecules of sodium alcoholate; 3) 2-dihydroxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 1000 molecules C_2H_5ONa.

Comparison of the data on the size of the shift of the α_2" band in 2-hydroxy- and 2,6-dihydroxyacetophenone occasioned by the alkali, as compared with its position in a neutral alcoholic solution (the maximum is shifted 430 and 375 A, respectively), indicates that salt formation at the second ortho hydroxyl group causes an additional shift of 50 A, i.e., 7-8 times less than the formation of a salt at the first hydroxyl group. In this respect, 2,6-dihydroxyacetophenone differs from 3,5 dihydroxyacetophenone, in which [1] the shift of the α_2" band due to the presence of 1000 molecules of sodium alcoholate is nearly 3 times as great as its shift in 3-hydroxyacetophenone.

Comparison of the absorption curves of 2,6- and 3,5-dihydroxyacetophenone when an excess of sodium alcoholate is present indicates that the absorption of the former is located at longer wavelengths than that of the latter. The maximum of the α_2" band of 2,6-dihydroxyacetophenone, for example, is shifted 340 A, compared to 3,5-dihydroxyacetophenone, and that of the α_1' band by 55 A. This shift exceeds the shift observed in neutral alcohol (especially as far as the α_2" band is concerned), where the band maxima are located at 3425 and 2275 A in 2,6-dihydroxyacetophenone and at 3210 and 2180 A in 3,5-dihydroxyacetophenone.

2-Hydroxy-6-methoxy-acetophenone in alcoholic solutions of sodium alcoholate. 2-Hydroxy-6-methoxyacetophenone was investigated in alkaline solutions of the following concentrations: 10^{-3}, 10^{-4}, and $4\cdot10^{-5}$ mol., with 1000 molecules of sodium alcoholate per mol of the substance. The absorption curve (Table 9; Fig. 6, Curve 2) starts at $\varepsilon = 100$ and $\lambda = 4150$ A and rises at a slant toward the shorter wavelengths, exhibiting a band with a maximum at $\lambda = 3420$ A and $\varepsilon = 5000$. The shortwave side of this band drops down to a minimum at $\lambda = 3035$ A and $\varepsilon = 1000$. Then the curve rises again to a second band with a maximum at $\lambda = 2780$ A and $\varepsilon = 6000$. After passing through a second minimum at $\lambda = 2595$ A and $\varepsilon = 1300$, the curve exhibits a third band, with a maximum at $\lambda = 2350$ A and $\varepsilon = 15000$.

TABLE 9

2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $4 \cdot 10^{-5}$ in alcohol + 1000 molecules of sodium alcoholate

λ		ε
4150		100
3480		4000
3420	maximum	5000
3360		4000
3100		1300
3035	minimum	1000
2970		1300
2800		5000
2780	maximum	6000
2760		5000
2620		1600
2595	minimum	1300
2570		1600
2370		12500
2350	maximum	15000
2330		12500
2290		10000

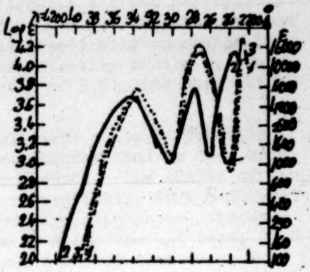


Fig. 6.

1) 2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $4 \cdot 10^{-5}$ mol., in alcohol; 2) 2-hydroxy-6-methoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 1000 molecules C_2H_5ON 3) 2-hydroxy-6-methoxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol in alcohol + 4000 molecules HCl.

The data on the absorption band maxima of 2-hydroxy-6- methoxy- and 2,6-dihydroxyacetophenone in alkaline solutions are listed in Table 10.

TABLE 10

Compound	α_2'' Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
2-Hydroxy-6-methoxyacetophenone in alcohol	3355	6000	2705	15000	2255	15000
2-Hydroxy-6-methoxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	3420	5000	2780	6000	2350	15000
2,6-Dihydroxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	3855	6000	2875	10000	2415	13000

As we see from the data in Table 10, as well as from a comparison of the curves shown in Fig. 6, the presence of sodium alcoholate in excess causes the following changes in the absorption curve of 2-hydroxy-6-methoxyacetophenone in neutral alcohol: a) The whole absorption curve is shifted toward the longer wavelengths, though the same absorption bands are preserved. The longwave edge of the α_2'' band is shifted 270 A at ε = 100 and 140 A at ε = 1000, the band maximum being shifted 65 A. The longwave edge of the α_1 band, on the other hand, is shifted somewhat toward the shorter wavelengths, while the shortwave edge of this band is shifted considerably toward the longer wavelengths (200 A at ε = 2500).

This causes a narrowing of the band; its maximum is shifted 75 A toward the longer wavelengths. The longwave edge of the α_1' band is likewise shifted perceptibly (the maximum being shifted by 95 A), as are the minima, particularly the minimum between the α_1 and α_1' bands (by 215 A); b) There is practically no change in the band intensity (except in the α_1 band). The band intensity in the α_1 band drops considerably in an alkaline solution (by a factor of 2.5), the absorption at the second minimum increasing 60%, however.

As we see from the foregoing, an excess of alkali acts quite differently, quantitatively speaking, upon 2-hydroxy-6-methoxyacetophenone than it does upon 2,6-dihydroxy-, 2-hydroxyacetophenone, and similar compounds. The shifts of the α_2", α_1, and α_1' bands totaled 430, 185, and 140 A, respectively, in 2,6-dihydroxyacetophenone, and 375 A for the α_2" band in 2-hydroxyacetophenone, whereas these shifts in 2-hydroxy-6-methoxyacetophenone were 65 A for the α_2" band, 75 A for the α_1 band, and 95 A for the α_1' band, i.e., some 6 to 6.5 times less for the α_2" band. As a result, the difference between the absorption curves of 2-hydroxy-6-methoxy- and 2,6-dihydroxyacetophenone is much greater than that in alcoholic solutions. Whereas the maximum of the latter's α_2" band in alcohol is located at $\lambda = 3425$ A, i.e., shifted 70 A toward the longer wavelengths from its position in the former compound, this shift is as much as 235 A in the alkaline solution. Though the positions of the two other bands are basically the same in the two compounds in neutral alcohol as in the alkaline solutions, in the 2,6-dihydroxyacetophenone they, like the α_2" band, are shifted toward the longer wavelengths, though to a much lesser extent.

2,6-Dimethoxyacetophenone in alcoholic solutions of sodium alcoholate. 2,6-Dimethoxyacetophenone was investigated spectrographically in alcoholic solutions of the following concentrations: 10^{-3} and 10^{-4} mol., with 1000 molecules of sodium alcoholate. As we see from Fig. 7 (Curve 2), the absorption curve starts at $\varepsilon = 1000$ and $\lambda = 3440$ A and, slanting upward, forms a band with a maximum at $\lambda = 2795$ A and $\varepsilon = 4000$. The shortwave edge of this band drops down to a minimum at $\lambda = 2670$ A and $\varepsilon = 1600$, after which the curve again rises to form a band with a maximum at $\lambda = 2565$ A and $\varepsilon = 4000$. After another minimum at $\lambda = 2405$ A and $\varepsilon = 1000$, the curve rises and breaks off at $\lambda = 2250$ A and $\varepsilon = 3500$.

TABLE 11

Compound	φ-Band		α_1 Band	
	λ	ε	λ	ε
2,6-Dimethoxyacetophenone in alcohol	2810	4000	2555	4000
2,6-Dimethoxyacetophenone in alcohol + 1000 molecules of sodium alcoholate	2795	4000	2565	4000

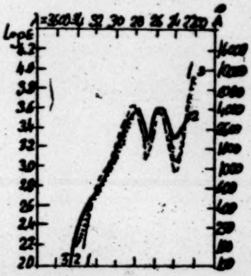


Fig. 7.

1) 2,6-Dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol; 2) 2,6-dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 1000 molecules of C_2H_5ONa; 3) 2,6-dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 4000 molecules of HCl.

Comparing the absorption curves of 2,6-dimethoxyacetophenone in alcohol and in an alcoholic solution of sodium alcoholate (Fig. 7), we see that they nearly coincide. As the data listed in Table 11 indicate, the band maxima are located at almost the same λ and ε. Merely the absorption intensity at the minima is somewhat greater in the alkali (by 25%).

The absence of change in the absorption curve of 2,6-dimethoxyacetophenone when sodium alcoholate is present supports the conclusion that the significant changes in the absorption curve observed in 2,6-dihydroxy- and 2-hydroxy-6-methoxyacetophenone in this solution are due to salt formation.

2,6-Dihydroxy-, 2-hydroxy-6-methoxy-, and 2,6-dimethoxyacetophenone in alcoholic solutions of HCl. We investigated 2,6-dihydroxyacetophenone in alcoholic solutions of HCl of the following concentration: 10^{-3} and 10^{-4} mol. with 4000 molecules of HCl per molecule of the substance, and 10^{-4} mol with 40,000 mol. of HCl per molecule of the substance.

The absorption curve in the solution containing 4000 molecules of HCl (Table 12; Fig. 8, Curve 2) starts at $\varepsilon = 100$ and $\lambda = 3900$ A. It consists of three bands with maxima at $\lambda = 3430$ A and $\varepsilon = 5000$; $\lambda = 2705$ A and $\varepsilon = 13000$; and $\lambda = 2255$ A and $\varepsilon = 13000$, respectively.

The presence of 40000 molecules of HCl causes the curve to suffer minor changes compared to the curve recorded when 4000 molecules of HCl are present.

As we see from Table 13 and Fig. 8, there is but little difference between the absorption curves in alcohol and in an alcoholic solution of HCl. The band maxima are located at the same λ and ε. The minima likewise coincide. It is only the longwave edge of the α_2" band that is shifted appreciably toward the longer wavelengths when HCl is present (by 150 A at $\varepsilon = 100$), but at $\varepsilon = 400$ it again coincides with the curve for the neutral alcohol solution.

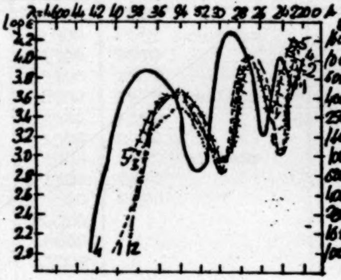


Fig. 8.

1) 2,6-Dihydroxyacetophenone, 10^{-3} - $6 \cdot 10^{-5}$ mol., in alcohol; 2) 2,6-dihydroxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 4000 molecules of HCl; 3) 2,6-dihydroxyacetophenone, 10^{-4} in alcohol + 40,000 molecules HCl; 4) 2,6-dihydroxyacetophenone 10^{-3} - $3 \cdot 10^{-5}$ mol., in concentrated H_2SO_4; 5) 2,6-dihydroxyacetophenone, 10^{-4} - $6 \cdot 10^{-5}$ mol., in 10% H_2SO_4.

We investigated 2-hydroxy-6-methoxy acetophenone spectrographically in alcoholic HCl solutions of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mol., containing 4000 molecules of HCl per molecule of the substance. The absorption curve (Table 12; Fig. 6, Curve 3) starts at $\varepsilon = 100$ and $\lambda = 3950$ A and rises, forming a band with a maximum at $\lambda = 3350$ A and $\varepsilon = 5000$. Dropping down to a minimum at $\lambda = 3040$ and $\varepsilon = 1000$, the curve again rises to form a α_1 band with a maximum at $\lambda = 2700$ A and $\varepsilon = 16600$. The curve has a third band in the shortwave region, with a maximum at $\lambda = 2260$ A and $\varepsilon = 20000$.

As we see from Fig. 6 and Table 13, the presence of the HCl causes no significant change in the absorption of the compound in neutral alcohol. The curves for both solutions practically coincide. We merely find slight changes in the positions of the absorption bands, which lie within the limits of experimental error in several instances.

We investigated the 2,6-dimethoxyacetophenone in alcoholic HCl solutions of

TABLE 12

2,6-Dihydroxyacetophenone 10^{-3}-10^{-4} mol., in alcohol + 4000 molecules of HCl			2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol. in alcohol + 4000 molecules of HCl			2,6-Dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol + 4000 molecules of HCl		
λ		ε	λ		ε	λ		ε
3900		100	3950		100	3460		100
3480		4000	3380		4000	2810		3500
3430	maximum	5000	3350	maximum	5000	2795	maximum	4000
3380		4000	3320		4000	2780		3500
3040		800	3140		1300	2680		2000
2985	minimum	700	3040	minimum	1000	2665	minimum	1600
2930		800	2940		1300	2650		2000
2760		10000	2750		13300	2600		3500
2705	maximum	13000	2700	maximum	16600	2575	maximum	4000
2650		10000	2650		13300	2550		3500
2485		1300	2470		1300	2440		1300
2430	minimum	1000	2415	minimum	1000	2405	minimum	1000
2380		1300	2360		1300	2370		1300
2270		10000	2270		16600	2190		10000
2255	maximum	13000	2260	maximum	20000			
2240		10000	2250		16600			
2180		8000	2230		10000			

TABLE 13

Compound	α_2'' band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
2,6-Dihydroxyacetophenone in alcohol ..	3425	5000	2690	13300	2275	13000
2,6-Dihydroxyacetophenone in alcohol + 4000 molecules of HCl	3430	5000	2705	13000	2255	13000
2,6-Dihydroxyacetophenone in alcohol + 40000 molecules of HCl	3415	3500	2695	13000	–	–
2-Hydroxy-6-methoxyacetophenone in alcohol	3355	6000	2705	15000	2255	15000
2-Hydroxy-6-methoxyacetophenone in alcohol + 4000 molecules of HCl	3350	5000	2700	16600	–	–
2,6-Dimethoxyacetophenone in alcohol ..	φ-Band 2810	4000	2555	4000	–	–
2,6-Dimethoxyacetophenone in alcohol + 4000 molecules of HCl	2795	4000	2575	4000	–	–

the following concentrations: 10^{-3} and 10^{-4} mol with 4000 molecules HCl per molecule of the substance. Comparing the absorption curves shown in Fig. 7, we see that here, too, the presence of HCl has no significant effect upon absorption.

2,6-Dihydroxyacetophenone in concentrated sulufric acid and sulfuric acid diluted with water. 2,6-Dihydroxyacetophenone dissolves in concentrated sulfuric acid, yielding a bright yellow solution. We investigated solutions of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mol. The absorption curve (Table 14; Fig. 8, Curve 4) starts at $\varepsilon = 100$ and $\lambda = 4260$ A and rises fairly steeply,

TABLE 14

2,6-Dihydroxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol., in concentrated sulfuric acid		2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $3 \cdot 10^{-5}$ mol., in concentrated sulfuric acid		2,6-Dimethoxyacetophenone, 10^{-3} - $6 \cdot 10^{-5}$ mol., in concentrated sulfuric acid	
λ	ε	λ	ε	λ	ε
4260	100	4425	100	4800	100
3770	6600	3800	6000	4050	5000
3700 maximum	8300	3725 maximum	7000	3910 maximum	6000
3630	6600	3650	6000	3770	5000
3270	800	3330	1000	3380	700
3220 minimum	700	3265 minimum	800	3320 minimum	600
3170	800	3200	1000	3260	700
2960	16600	2990	20000	3080	16600
2890 maximum	18300	2950 maximum	25000	3010 maximum	20000
2820	16600	2910	20000	2940	16600
2620	2150	2610	1000	2540	500
2585 minimum	1660	2590 minimum	800	2500 minimum	400
2550	2150	2570	1000	2460	500
2430	10000	2400	13300	2140	8000
2415 maximum	11500	2390 maximum	16600		
2400	10000	2380	13300		
2310	5000	2370	11600		
2300 minimum	4130				
2290	5000				
2180	11500				

TABLE 15

Compound	α_2' Band		φ-Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
2,6-Dihydroxyacetophenone in alcohol	3425	5000	–	–	2690	13300	2275	13000
2,6-Dihydroxyacetophenone in 10% sulfuric acid	3410	5000	–	–	2705	11600	2275	18300
2,6-Dihydroxyacetophenone in concentrated sulfuric acid	3700	8300	2890	18300	–	–	2415	11500
Acetophenone in concentrated sulfuric acid	3300	2400	2950	20500	–	–	–	–
3,5-Dihydroxyacetophenone in concentrated sulfuric acid	3730	4000	3035	13750	–	–	2280	12500

forming a wide band, with a maximum at λ = 3700 A and ε = 8300. Dropping to a minimum at λ = 3220 A and ε = 700, the curve rises again to form a second, very strong band, with a maximum at λ = 2890 A and ε = 18300. The maximum of the third band of the curve is located at λ = 2415 A and ε = 11500. The minimum between the latter two bands is located at λ = 2585 A and ε = 1660. The curve exhibits a third minimum in the shortwave region of the spectrum, at λ = 2300 A and ε = 4130. After this minimum, the curve rises and breaks off at λ = 2180 A and ε = 11500.

The data on the absorption band maxima of 2,6-dihydroxyacetophenone in alcohol, concentrated sulfuric acid, and sulfuric acid diluted with water, as well as of unsubstituted acetophenone in concentrated sulfuric acid, according to Flexer, Hammet, and Dingwall [19], are listed in Table 15.

Inspection of the absorption curves (Fig. 8) and of the data in Table 15 indicates that 2,6-dihydroxyacetophenone possesses a wide band in the longwave region both in alcohol and in concentrated sulfuric acid. This band in the concentrated sulfuric acid is like the band in alcoholic solution, and apparently is the α_2'' band, shifted toward the longer wavelengths and made somewhat stronger as the result of the acid's action. The band with a maximum at $\lambda = 2415$ A is apparently the α_1' band in alcohol shifted toward the longer wavelengths. The absorption changes occurring in the α_1 band as the result of the acid's action are more significant, as we noted in various hydroxy- and methoxy-substituted acetophenones investigated earlier [1,18]. The α_1 band does not exist on the curve for the acid. Shifted toward the longer wavelengths, it falls within the region of a new and quite strong band – the φ band – located at nearly the same λ and ε as in the curve for unsubstituted acetophenone in the same acid. Evidently, the acid causes a large drop in the absorption intensity in the region of the α_1 band and a sharp rise in absorption intensity in the region of the acetophenone φ band, both in 2,6-dihydroxyacetophenone and (according to Flexer, Hammet, and Dingwall [19]) in acetophenone.

Comparison of the data on the absorption curves of 2,6- and 3,5-dihydroxyacetophenone indicates that concentrated sulfuric acid has the same effect in both instances. The curves exhibit the same three bands: α_2'', φ, and α_1', and their α_2'' bands are located at nearly the same λ.. In the 2,6-dihydroxy compound its maximum is shifted 30 A toward the shorter wavelengths, while the absorption intensity rises nearly 100%. The maximum of the φ band is likewise shifted toward the shorter wavelengths (by 145 A) in 2,6-dihydroxyacetophenone, but in this region, too, the absorption intensity is higher than in the 3,5-dihydroxyacetophenone. In contrast to the α_2'' and φ bands, the α_1' band of 2,6-dihydroxyacetophenone is shifted 135 A toward the longer wavelengths, as against 3,5-dihydroxyacetophenone. Thus, though the absorption curve for 2,6-dihydroxyacetophenone is located at longer wavelengths in alcoholic solutions than is the curve for 3,5-dihydroxyacetophenone, especially in the α_2'' band (the maximum of which is shifted 215 A), conditions are reversed in concentrated sulfuric acid: it is the 3,5-dihydroxyacetophenone that absorbs at longer wavelengths. This is also seen in the fact that the longwave edge of the α_2'' band of 2,6-dihydroxyacetophenone is shifted 520 A at $\varepsilon = 100$ and 120 at $\varepsilon = 1000$ toward the shorter wavelengths, as compared with 3,5-dihydroxyacetophenone.

Diluting the 10^{-3} mol. solution in concentrated sulfuric acid to 10^{-4} mol. with water decolorizes the solution and eliminates the above-mentioned effect of sulfuric acid upon the absorption spectrum, as was the case in the other hydroxy and methoxyacetophenones investigated [1,18].

We investigated 10^{-4} and $6 \cdot 10^{-5}$ molar solutions spectrographically. The absorption curve (Table 16; Fig. 8, Curve 5) begins at $\varepsilon = 1000$ and $\lambda = 3850$ A and consists of three bands, whose maxima are located at the same values of λ as in the neutral solution. The curve for the solution in dilute sulfuric acid coincides with the curve in alcohol almost throughout its length. The longwave edge of the α_2'' band exhibits a certain shift toward the longer wavelengths. In the acid the absorption intensity also is increased somewhat at the second minimum.

2-Hydroxy-6-methoxyacetophenone in concentrated sulfuric acid and in sulfuric acid diluted with water. 2-Hydroxy-6-methoxyacetophenone dissolves in concentrated sulfuric acid, like 2,6-hydroxyacetophenone, forming a yellow solution. We investigated solutions of the following concentrations: 10^{-3}, 10^{-4}, and $3 \cdot 10^{-5}$ mol.

The absorption curve (Table 14, Fig. 9, Curve 2) starts at $\varepsilon = 100$ and $\lambda =$

TABLE 16

2,6-Dihydroxyacetophenone, 10^{-4} - $6 \cdot 10^{-5}$ mol., in 10% aqueous sulfuric acid		2-Hydroxy-6-methoxyacetophenone, 10^{-4} mol., in 10% aqueous sulfuric acid		2,6-Dimethoxyacetophenone, 10^{-4} mol., in 10% sulfuric acid	
λ	ε	λ	ε	λ	ε
3850	1000	3770	1000	3070	1000
3500	4000	3400	6000	2810	4000
3410 maximum	5000	3325 maximum	7000	2795 maximum	5000
3320	4000	3250	6000	2780	4000
3020	1000	3090	2500	2700	2000
2960 minimum	800	3060 minimum	2000	2685 minimum	1600
2900	1000	3030	2500	2670	2000
2740	10000	2800	10000	2620	3500
2705 maximum	11600	2710 maximum	13000	2600 maximum	4000
2670	10000	2620	10000	2580	3500
2520	2500	2490	3000	2440	1000
2495 minimum	2000	2475 minimum	2500	2390 minimum	800
2470	2500	2460	3000	2340	1000
2290	16600	2390	10000	2140	5000
2275 maximum	18300	2400	13300		
2260	16600	2390 maximum	16600		
2220	11600	2380	13300		
		2370	11600		

4425 A and rises, with a slight slope toward the shorter wavelengths, to form a wide band, with a maximum at λ = 3725 A and ε = 7000. This band is parallel to the similar band in the longwave region of the spectrum in neutral alcohol and is the α_2'' band, shifted toward the longer wavelengths by the acid. Dropping to a minimum at λ = 3265 A and ε = 800, the curve rises again to form a very strong band with a maximum at λ = 2950 A and ε = 25000. As we have stated above, this band corresponds to the φ band in acetophenone. After a second minimum at λ = 2590 A and ε = 800, the curve exhibits one more band, parallel to the α_1' band of 2-hydroxy-6-methoxyacetophenone in alcohol, with a maximum at λ = 2390 A and ε = 16600.

Comparison with the absorption curve in alcohol and with the data listed in Table 17 indicates that the acid does not affect the nature of absorption in the α_2'' and α_1' bands. In the acid these bands are shifted nearly in parallel toward the longer wavelengths, with only a slight increase in intensity. The longwave edge of the α_2'' band is shifted 545 A at ε = 100 and 440 A at ε = 1000, for instance, while the band maximum is shifted 370 A, the longwave edge of the α_1' band is shifted in the same direction by 170 A at ε = 800, the band maximum being shifted 135 A.

Apparently, the α_1 band is likewise shifted toward the longer wavelengths. The band with a maximum at λ = 2950 A is not the α_1 band of the absorption curve in alcohol, however. As has been pointed out above, this band is like the φ band in unsubstituted acetophenone. In 2-hydroxy-6-methoxyacetophenone it is located at the same λ as in acetophenone (at λ = 2950). and at nearly the same ε (20% higher in 2-hydroxy-6-methoxyacetophenone). The data on acetophenone in sulfuric acid solutions of various concentrations indicate that this is a complex band, consisting of the φ band proper of acetophenone, greatly increased in intensity, and of the α_1 band shifted into its absorption region.

In comparison to 2,6-dihydroxyacetophenone, the presence of acid causes a

TABLE 17

Compound	α_2" Band		φ-Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
2-Hydroxy-6-methoxyacetophenone in alcohol	3355	6000	–	–	2705	15000	2255	15000
2-Hydroxy-6-methoxyacetophenone in 10% sulfuric acid	3325	7000	–	–	2710	13000	–	–
2-Hydroxy-6-methoxyacetophenone in concentrated sulfuric acid	3725	7000	2950	25000	–	–	2390	16600
2,6-Dihydroxyacetophenone in concentrated sulfuric acid	3700	8300	2890	18300	–	–	2415	11500

somewhat greater shift of absorption toward the longer wavelengths in 2-hydroxy-6-methoxyacetophenone. In comparison to alcoholic solutions, for instance, the shift of the α_2" band is 275 A in the former and 370 A in the latter. This effaces the differences in the absorption curves of the compounds in question. The position of the maximum changes less than in alcohol (for the α_2" band), the difference being 25 A; the α_1' band occupies the same position, though its intensity has risen 40% and its maximum is slightly shifted toward the shorter wavelengths (by 25 A). The long-wave edge of the α_2" band is shifted appreciably toward the longer wavelengths in 2-hydroxy-6-methoxyacetophenone, compared to the curve for 2,6-dihydroxyacetophenone (165 A at $\varepsilon = 100$, for instance). The φ band is likewise shifted in that direction (its maximum by 60 A), while its intensity increases 40%, and the first minimum is also shifted (by 45 A); the absorption intensity is nearly halved at the second minimum of 2-hydroxy-6-methoxyacetophenone.

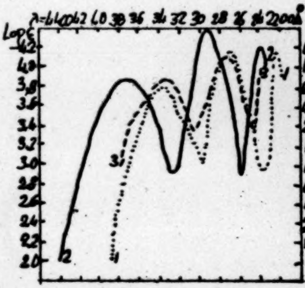


Fig. 9.

1) 2-Hydroxy-6-methoxyacetophenone, 10^{-3} - $4\cdot10^{-5}$ mol., in alcohol, 2) 2-hydroxy-6-methoxyacetophenone, 10^{-3} - $3\cdot10^{-5}$ mol., in concentrated H_2SO_4; 3) 2-hydroxy-6-methoxyacetophenone, 10^{-4} mol., in 10% H_2SO_4.

Diluting a 10^{-3} molar solution in concentrated sulfuric acid to a 10^{-4} molar solution with water wholly eliminates the above-mentioned effect of the acid upon absorption, as was the case in the 2,6-dihydroxyacetophenone. The absorption curve starts at $\varepsilon = 1000$ and $\lambda = 3770$ A (Table 16; Fig. 9, Curve 3) and rises to form two bands with maxima at $\lambda = 3325$ A and $\varepsilon = 7000$ and $\lambda = 2710$ A and $\varepsilon = 13000$. As we see in Table 17 and in Fig. 9, dilution restores the spectrum of the compound in alcoholic solution almost entirely, with slight changes in the location of the bands (the α_2" band is shifted 30 A toward the shorter wavelengths, etc.). The changes at the band minima are somewhat greater. The minima are shifted toward the longer wavelengths: the first one by 75 A and the second by 95 A, their absorption intensity increasing by a factor of 2 to 3.

2,6-Dimethoxyacetophenone in concentrated sulfuric acid and in sulfuric acid diluted with water. 2,6-Dimethoxyacetophenone dissolves in concentrated sulfuric acid, forming a yellow solution, as was the case in the compounds investigated previously. Solutions of 10^{-3}, 10^{-4}, and $6 \cdot 10^{-5}$ molar concentrations were investigated spectrographically.

The curve (Table 14) starts at $\varepsilon = 100$ and $\lambda = 4800$ A and rises, with a slight slope, toward the shorter wavelengths, to a wide band with a maximum at $\lambda = 3910$ A and $\varepsilon = 6000$. After a deep minimum at $\lambda = 3320$ A and $\varepsilon = 600$, the curve rises again to exhibit a second, very strong band with a maximum at $\lambda = 3010$ A and $\varepsilon = 20000$. Then the curve drops down again to a minimum at $\lambda = 2500$ A and $\varepsilon = 400$ and, rising, breaks off at $\lambda = 2140$ A and $\varepsilon = 8000$. Comparison with the absorption curves of 2,6-dihydroxy- and 2 hydroxy-6-methoxyacetophenone as well as unsubstituted acetophenone in sulfuric acid indicates that the first band exhibited by 2,6-dimethoxyacetophenone in the acid is a α_2'' band, and the second a φ band.

Comparison of the absorption curves in acid and in alcohol (Fig. 10, Curves 1 and 2) plus the data in Table 18 indicate that the acid causes a marked change in absorption. Whereas the α_2'' band is not manifested in alcohol, it develops into a very wide band in the acid, with an intensity that approaches that of the other compounds discussed in the present paper. The φ band, which is narrow and relatively weak in alcohol, develops into a highly intense band (ε increases fivefold). As against the curve in the alcoholic solution, this band is shifted 200 A toward the longer wavelengths. The α_1 band of the alcoholic solution is not manifest in the presence of acid, as was the case in the other compounds tested (vide supra). Apparently, it is again shifted toward the longer wavelengths and falls within the absorption region of the φ band.

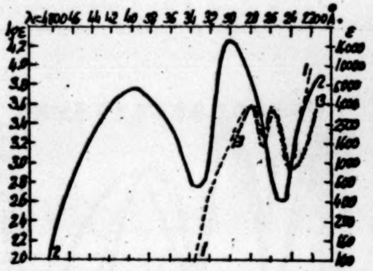


Fig. 10.

1) 2,6-Dimethoxyacetophenone, 10^{-3} - 10^{-4} mol., in alcohol; 2) 2,6-dimethoxyacetophenone, 10^{-3} - $6 \cdot 10^{-5}$ mol., in concentrated H_2SO_4; 3) 2,6-dimethoxyacetophenone 10^{-4} mol., in 10% H_2SO_4.

In concentrated sulfuric acid, the absorption curve of 2,6-dimethoxyacetophenone has the same shape as the curves for 2,6-dihydroxy- and 2-hydroxy-6-methoxyacetophenone in the same medium, in contrast to what we observed in alcoholic solutions. As is readily seen in Fig. 11, all three curves have the same α_2'' and φ bands, which run parallel to one another. It is worthy of note that as the hydroxyl groups of 2,6-dihydroxyacetophenone are methylated, the absorption of the resulting compound in concentrated sulfuric acid in the region of the α_2'' band is progressively shifted toward the longwave region while the absorption intensity is diminished somewhat. This band undergoes a particularly large shift when both of the hydroxyl groups are methylated (by 185 A). The φ band is likewise progressively shifted toward the longer wavelengths as the hydroxyl groups are methylated, the sole difference being that methylation of each hydroxyl group entails an equal shift of the band (60 A). Moreover, in 2,6-dimethoxyacetophenone, the intensity of the φ band drops below that of 2-hydroxy-6-methoxyacetophenone, to the value it has in unsubstituted acetophenone. In contrast to the compounds specified, the absorption intensity is sharply diminished at the second minimum in 2,6-dimethoxyacetophenone (a fivefold drop compared to the 2,6-dihydroxy compound, and a 50% drop compared to 2-hydroxy-6-methoxyacetophenone), while the minimum itself is shifted 90 A toward the shorter wavelengths.

TAPLE 18

Compound	α_2'' Band		φ - Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
2,6-Dimethoxyacetophenone in alcohol	–	–	2810	4000	2555	4000	–	–
2,6-Dimethoxyacetophenone in 10% sulfuric acid	–	–	2795	5000	2600	4000	–	–
2,6-Dimethoxyacetophenone in concentrated sulfuric acid	3910	6000	3010	20000	–	–	–	–
2-Hydroxy-6-methoxyacetophenone in concentrated sulfuric acid	3725	7000	2950	26600	–	–	2390	16600
2,6-Dihydroxyacetophenone in concentrated sulfuric acid	3700	8300	2890	18300	–	–	2415	11500
Acetophenone in concentrated sulfuric acid	3300	2400	2950	20500	–	–	–	–

The similarity of the sulfuric-acid absorption curves of these compounds indicates that the acid wipes out the previously noticed effect of methylating the two hydroxyl groups in 2,6-dihydroxyacetophenone.

The identical nature of the effect of concentrated sulfuric acid upon the compounds investigated in the present research is also seen in the fact that diluting a 10^{-3} molar solution of 2,6-dimethoxyacetophenone in concentrated sulfuric acid to 10^{-4} mol. with water restores the type of absorption exhibited in neutral media or in the presence of HCl. The absorption curve (Table 18; Fig. 10, Curve 3) starts at $\varepsilon = 1000$ and $\lambda = 3070$ A and exhibits the same two bands as in the alcoholic solution. The maxima of these bands are located at $\lambda = 2795$ A and $\varepsilon = 5000$ and $\lambda = 2600$ A and $\varepsilon = 4000$, that is, the first one is shifted 15 A toward the shorter wavelengths, and the second 45 A toward the longer wavelengths.

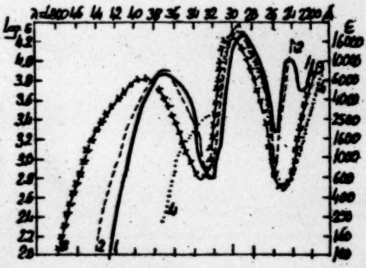
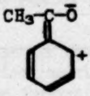
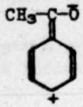


Fig. 11.

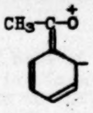
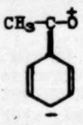
1) 2,6-Dihydroxyacetophenone, 10^{-3} - $3\cdot10^{-5}$ mol., in concentrated H_2SO_4; 2) 2-hydroxy-6-methoxyacetophenone, 10^{-3} - $3\cdot10^{-5}$ mol., in concentrated H_2SO_4; 3) 2,6-dimethoxyacetophenone, 10^{-3} - $6\cdot10^{-5}$ mol., in concentrated H_2SO_4; 4) acetophenone in concentrated H_2SO_4.

Evaluation of the Absorption Spectra

Our investigation of the absorption spectra of acetophenone and its hydroxy and methoxy derivatives has led us to conclude that the molecules of these compounds can exist in two states: the α and the φ state; the first of these is characterized by joint cojugation, and the second by individual conjugation, of the $COCH_3$ and OH or OCH_3 groups with the double bonds of the benzene ring. Joint conjugation promotes the development of structure of the carbonium type:

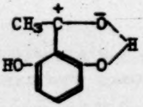
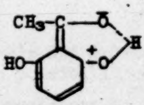



Individual conjugation promotes the development of structures of the oxonium type:

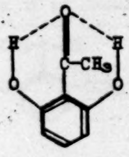



In the α state the molecules cause absorption in the α_2 and α_1 bands, while in the φ state they cause absorption in the φ band. Moreover, the presence of OH or OCH_3 groups in the molecule may tend to shift the equilibrium between the α and φ states in one direction or the other, thus exhibiting spectra of the α or φ type.

Spectra of the α type predominate in 2-hydroxyacetophenone, due to the presence of an intramolecular hydrogen bond. In 2,6-dihydroxyacetophenone the spectrum of the α type is reinforced still further, this being due, apparently, to an increase in the strength of its hydrogen bond. That such a bond is present in 2,6-dihydroxyacetophenone is proved by its displaying the physical properties that are characteristic of such compounds: rather free solubility in hexane, sparing solubility in water, and color. It is these properties that distinguish 2,6-dihydroxyacetophenone from its isomer, 3,5-dihydroxyacetophenone. The presence of an intramolecular hydrogen bond in the former compound is obviously responsible for some of its anomalous chemical properties: failure to yield a hydrazone [3], low velocity of the acetylation reaction [20], etc. A more stable hydrogen bond would have involved a greater displacement of the hydrogen in the OH group to the oxygen of the carbonyl group, i.e., a greater asymmetry of the hydrogen bridge: O-H...O=C [21]. The participation of the OH^- and C=O groups in the formation of the hydrogen bond reinforces their mutually complementary electromeric effect. Since the hydrogen bond fixes the double bond of the benzene ring between the carbon atoms to which the groups participating in the formation of the bridge are attached, according to Baker [22], the presence of intramolecular association in 2,6-dihydroxyacetophenone signifies the formation of the following carbonium structures:

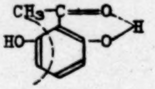



The further development of the α state in 2,6-dihydroxyacetophenone might also be due to the formation of a hydrogen bond with the second ortho hydroxyl group:



This is not borne out by the spectrographic behavior of these compounds, however.

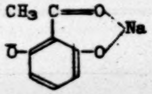
A certain increase in the absorption in the φ band in 2,6-dihydroxyacetophenone over that in 2-hydroxyacetophenone is an indication of the presence of individual conjugation in the former as well.



Esterification of both of the hydroxyl groups of 2,6-dihydroxyacetophenone causes a sharp change in the spectrum, the absorption being weakened in the bands that are characteristic of the α state and strengthened in the φ band, the spectrum approaching that of 1,3-dimethoxybenzene. This change is apparently caused by a marked weakening of the conjugation of the acetyl group with the benzene ring, as well as by the elimination of any possibility for the formation of a hydrogen bond within the molecule. As a result, all we find is individual conjugation of the methoxy groups with the benzene ring, and the absorption curve of 2,6-dimethoxyacetophenone resembles that of 1,3-dimethoxybenzene, [23].

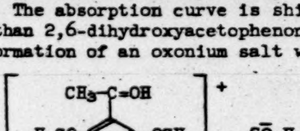
In alcohol, intermolecular hydrogen bonds are also formed with the alcohol molecules, causing a certain shift of absorption toward the longer wavelengths. This explains the shift of the α_2'' and α_1 bands toward the longer wavelengths in the previously investigated 2-hydroxy-, and 3,5-dihydroxyacetophenone and in their methyl esters. The absence of this shift in 2,6-dihydroxy- and 2-hydroxy-6-methoxyacetophenone is due to the fact that the association of the carbonyl group within the molecule renders it unable to establish an intermolecular hydrogen bond with the molecules of alcohol. In 2,6-dimethoxyacetophenone, which has no hydrogen bond within the molecule, the bands are shifted toward the longer wavelengths in alcoholic solution from the positions they occupy in a hexane solution, as was the case in the meta derivatives.

When sodium alcoholate is present, 2,6-dihydroxyacetophenone exhibits a marked shift of the absorption bands toward the longer wavelengths. This is the result of conjugation with the O^- ion, as well as, possibly, of the formation of molecules in which sodium participates in the association within the molecule at the concentrations tested:



Lifschitz [24], Hantzsch and Kraeber [25], Brady and Badger [26], Sidgwick and Brawer [27], and others have commented on the possibility of bridges of this type.

The absorption curve of 2,6-dimethoxyacetophenone in sulfuric acid proves to resemble the curve of 2,6-dihydroxyacetophenone, in contrast to what we found in hexane or in alcohol. The absorption curve is shifted in the acid toward the longer wavelengths more than 2,6-dihydroxyacetophenone's curve is in the same acid. Apparently, the formation of an oxonium salt with the acid:



restores the ability of the $COCH_3$ group to enter into conjugation with the benzene ring.

SUMMARY

1. A study has been made of the absorption spectra of 2,6-dihydroxy-, 2-hydroxy-6-methoxy, and 2,6-dimethoxyacetophenone in hexane, alcohol, alcoholic solutions of various amounts of sodium alcoholate and HCl, concentrated sulfuric acid, and sulfuric acid diluted with water.

2. It has been found that introducing a second hydroxy or methoxy group into 2-hydroxyacetophenone at the 6 position gives rise to spectra of chiefly the α type. Some development of φ type spectra is also observed.

3. The peculiarities of the absorption of 2,6-dihydroxyacetophenone are due to its possessing an intramolecular hydrogen bond. Only one of the ortho hydroxyl molecules participates at a time in the formation of this intramolecular hydrogen bond.

4. The formation of a salt at the second ortho hydroxyl group in 2,6-dihydroxyacetophenone has only a slight effect upon the absorption curve.

5. It has been shown that making it impossible for a hydrogen bond to be formed within the molecule produces a shift of the absorption curve toward the shorter wavelengths.

6. The absorption curve of 2,6-dihydroxyacetophenone is changed fundamentally by esterification. The curve of 2,6-dimethoxyacetophenone resembles the curve of the dimethyl ester of resorcinol.

7. The part played by the carbonyl group of 2,6-dimethoxyacetophenone in conjugation with the benzene ring is greatly diminished in various media. The conjugation of the acetyl group with the double bonds of the benzene ring is restored in concentrated sulfuric acid. Hence, many phenomena involving the so-called "steric hindrances" are evidently due to the elimination of the conjugation of groups with the benzene ring.

8. Some of the absorption singularities set forth above may be satisfactorily explained by the possibility of these compounds existing in two states: the α and the φ state, the first being characterized by the predominance of molecules with carbonium structure in the equilibrium, and the second by the predominance of molecules with oxonium structure.

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FREE RADICALS IN THE DECOMPOSITION REACTIONS OF BENZENEAZOTRIPHENYLMETHANE, NITROSOACETANILIDE, AND BENZENEAZOTRINITROMETHANE IN SOLUTIONS

G. A. Razuvaev and E. I. Fedotova

More and more attention is being attracted of late to the reactions produced by free radicals in the liquid phase. Besides the extremely great theoretical importance of an expansion of our concepts of the mechanism of chemical reactions, study of these processes is also of considerable practical value, inasmuch as these reactions include the phenomena of polymerization of unsaturated compounds, numerous addition reactions at multiple bonds, many oxidation processes, and so forth.

One of the principal methods of discovering and identifying radicals is the reactions involving their attachment to elements. This method is applicable in the gaseous as well as the liquid phase. That is how Waters proved that a phenyl radical was formed in the reaction of phenyldiazonium with Hg, Sb, As, and Te, also securing the phenyl derivatives of these elements; phenylmercury chloride was formed by decomposing nitrosoacetanilide in carbon tetrachloride with mercury present [1]. By attaching the phenyl radical to Hg, Sb, and Te, Sandin, McClure and Irwin [2] have proved that it is formed when diphenyliodonium chloride is heated. Razuvaev has demonstrated that the phenyl radical is formed when benzoyl peroxide is decomposed in a solution of carbon tetrachloride, by synthesizing phenylmercury chloride in this reaction. Wieland and his co-workers [3] suggested that the decomposition of benzeneazotriphenylmethane in solutions proceeds in accordance with the equation:

$$(C_6H_5)_3CN_2C_6H_5 \longrightarrow (C_6H_5)_3C\cdot + N_2 + C_6H_5\cdot .$$

The phenyl radical also reacts with solvents in the usual manner. The shift of the phenyl radical to elements has not been described hitherto; we therefore ran experiments in which benzeneazotriphenylmethane was decomposed in various organic solvents containing finely divided mercury. We found that organometallic derivatives were formed, but we were able to secure an individual substance – phenylmercury chloride – only in the carbon tetrachloride solution, i.e., under the same reaction conditions as those used for benzoyl peroxide or nitrosoacetanilide. The amount of phenylmercury chloride isolated in our experiments wase extremely small. Apparently, most of the phenyl radicals react with the solvent, only a small proportion colliding with the metallic mercury and combining with it. That is why we would very much have liked to employ a radical acceptor that was soluble in organic solvents. It seemed to us that diphenyltin might be such a substance. It might be converted into hexaphenylbistannane or tetraphenyltin. Reactions of this sort are employed to synthesize mixed tin compounds of the Alk_2SnAr_2 type. A dialkyltin adds Ar radicals when it is heated with Ar_2Hg [4]. More highly phenylated compounds might possibly be formed in a disproportionation reaction:

$$3(C_6H_5)_2Sn \longrightarrow 2(C_6H_5)_3Sn + Sn; \qquad 4(C_6H_5)_3Sn \longrightarrow 3(C_6H_5)_4Sn + Sn,$$

but then metallic tin ought to be recovered.

We prepared hexaphenylbistannane by heating a benzene solution of benzeneazotriphenylmethane with diphenyltin. Absolutely no tin was recovered: hence, the reaction involved the addition of the phenyl radical to the diphenyltin:

$$(C_6H_5)_3CN_2C_6H_5 \longrightarrow (C_6H_5)_3C\cdot + N_2 + C_6H_5\cdot; \quad (C_6H_5)_2Sn + C_6H_5\cdot \rightarrow (C_6H_5)_3Sn\cdot .$$

We undertook to discover whether diphenyltin could not be used as a fixative for the phenyl radicals during the decomposition of nitrosoacetanilide in solutions. In this case, the reaction is complicated by the appearance of the CH_3CO_2 radical, which readily acetylates metals, as we know, and ought to react with the diphenyltin, converting it into a tetravalent derivative of diphenyltin.

$$C_6H_5N(NO)COCH_3 \longrightarrow C_6H_5\cdot + N_2 + CH_3CO_2\cdot \quad ;$$

$$2CH_3CO_2\cdot + (C_6H_5)_2Sn \rightarrow (C_6H_5)_2Sn(CO_2CO_3)_2.$$

At the same time, however, we succeeded in recovering a small quantity of tetraphenyltin, formed by the addition of phenyl radicals to diphenyltin. It was still unclear why tetraphenyltin was formed in this reaction rather than a hexa aryl bistannane, as in the decomposition of benzeneazotriphenylmethane. No tetraphenyltin was found when the latter was heated in benzene solution with hexaphenylbistannane. When nitrosoacetanilide was reacted with hexaphenylbistannane in carbon tetrachloride, triphenyltin chloride was found among the reaction products. What probably happened was that the triphenyltin reacted with the carbon tetrachloride in the presence of the free radicals formed by the decomposition of the nitrosoacetanilide. One of the present authors noticed a similar reaction when carbon tetrachloride was reacted with diphenylmercury in the presence of benzoyl peroxide; this yielded phenylmercury chloride.

We were interested in effecting decomposition reactions of benzeneazotrinitromethane in various solvents. According to the literature [5], this substance is a yellow powder that is highly explosive and decomposes readily in solutions. It might have been supposed that it would decompose, like benzeneazotriphenylmethane, as follows:

$$C_6H_5N_2C(NO_2)_3 \longrightarrow C_6H_5\cdot + N_2 + C(NO_2)_3\cdot \quad .$$

No diphenyl was discovered in the reactions with benzene nor diphenyl in the ethylcellosolve solution, as should have been the case if the phenyl radical had been present. Nor were we able to isolate any organometallic compounds of mercury when we reacted mercury with carbon tetrachloride. We always recovered nitrophenols from the solvent used. Therefore, this reaction involves the oxidative nitration of the phenyl radical.

EXPERIMENTAL

Decomposition of benzeneazotriphenylmethane in butyl ether with mercury present. 5.0 g of the azo compound was dissolved in 30 ml of butyl ether. The solution was placed in a flask fitted with a reflux condenser, together with 150 g of mercury, which was divided into tiny drops by a powerful stirrer. The solution was gradually heated to boiling in a current of carbon dioxide; this heating lasted about 5 hours. At 70°, nitrogen began to be evolved vigorously, the solution turning reddish-orange. The mercury was removed, the solution filtered, and the ether driven off. The flask contained a tarry residue containing organometallic compounds of mercury, which could not be recovered in the pure state, however. When the residue was oxidized with a mixture of sulfuric and nitric acids, we secured a solution that contained the mercury ion, as proved by the usual reactions.

Decomposition of benzeneazotriphenylmethane in carbon tetrachloride. This experiment was run like the preceding one, using 10 g of the azo compound, 75 ml of carbon tetrachloride, and 200 g of mercury. After having been heated in a current of carbon dioxide, and the mercury removed, the filtered solution was distilled with steam. The tarry residue was extracted with hot acetone. As the acetone solution cooled, the characteristic crystals of phenylmercury chloride settled out; after washing with acetone they were fairly pure and had a m.p. of 252°.

Decomposition of a benzene solution of benzeneazotriphenylmethane with diphenyltin present. A solution of 3.0 g of the azo compound in 60 ml of benzene was heated with 6.0 g of diphenyltin in a current of carbon dioxide for 5 hours, with stirring. After heating was complete, a current of air was passed through the solution to convert the diphenyltin into benzene-insoluble oxides. The precipitate was filtered out of the solution, which was set aside to stand in air, large rhombic crystals of hexaphenylbistannane settling out. They were filtered out and recrystallized from benzene. This yielded 0.2 g of pure hexaphenylbistannane. The crystals rapidly turned dull when exposed to air, owing to their losing their crystallization benzene. The hexaphenylbistannane had a m.p. of 229° after having been kept for many days in a desiccator, and a sample exhibited no depression when mixed with the pure substance.

Similar results were secured in experiments using a carbon tetrachloride solution. No tin was recovered in any of the tests. No tetraphenyltin was formed when the reaction was carried out in benzene, using hexaphenylbistannane instead of diphenyl tin.

Decomposition of nitroscacetanilide dissolved in carbon tetrachloride with diphenyltin present. A solution of 2.0 g of nitrosoacetanilide and 3.0 g of diphenyltin in 65 ml of carbon tetrachloride was allowed to stand in an atmosphere of carbon dioxide until no more nitrogen was evolved. A precipitate settled to the bottom of the flask, which was filtered out. It was soluble in acetone; evaporation of the solvent yielded a light brown powder that deliquesced when exposed to the air. The filtered solution was concentrated, causing the precipitation of a light-yellow deposit, which was squeezed out on a porous plate and recrystallized from toluene. This yielded the snow-white crystals of tetraphenyltin, with a m.p. of 225°, exhibiting no depression when mixed with the pure substance.

Decomposition of nitrosoacetanilide dissolved in carbon tetrachloride with hexaphenylbistannane present. A solution of 1.2 g of the nitroso derivative and 1.5 g of hexaphenylbistannane in 60 ml of carbon tetrachloride was allowed to stand for 2 days in an atmosphere of carbon dioxide. The solution was then filtered and concentrated somewhat. When it was allowed to stand, crystals of triphenyltin chloride, with a m.p. of 101°, settled out. Recrystallization from benzene yielded 0.06 g of the pure chloride, with a m.p. of 103°. The mother liquor yielded crystals of the unreacted hexaphenylbistannane.

Decomposition of a benzene solution of benzeneazotrinitromethane. 15 g of benzeneazotrinitromethane was dissolved in 150 ml of benzene. The solution was set aside to stand, and a gas began to evolve, this evolution terminating toward the end of the fifth day. When the reaction was complete, the benzene was driven off in vacuum; the residue was distilled with steam, and a small quantity of o-nitrophenol, with a m.p. of 44°, was found in the distillate. A sample exhibited no depression when mixed with the pure preparation. The flask contained a tarry residue after the distillation was over. The dry residue weighed 9 g. Much of it dissolved in hot water. Yellow cubic crystals, with a m.p. of 65°, settled out of the aqueous extract. Recrystallization from alcohol yielded 2 g of a crystalline substance with a m.p. of 85°. The substance was soluble in water, turning it yellow, the color turning a deeper yellow when alkali was added. The substance contained nitrogen. All of its properties indicated that the substance was a nitrophenol. It probably was a mixture of p-nitrophenol (m.p. 113°, mol. wt. 139) and 2,4-dinitrophenol (m.p. 112-114°, mol. wt. 184). The determinations of the molecular weight and percentage of nitrogen yielded values in agreement with this assumption.

0.1473 g substance: 19.24 g C_6H_6: Δt 0.24°. 0.2966 g substance: 19.24 g C_6H_6: Δt 0.43°. Found: M 159.4; 166.6. 0.1807 g substance: 21.1 ml N_2 (20°, 743 mm). 0.2084 g substance: 25.4 ml N_2 (20°, 743 mm). Found %: N 13.1, 13.7. $C_6H_4O_5N_2$. Computed %: N 15.2. $C_6H_5O_3N$. Computed %: N 10.1.

No diphenyl was found in the reaction products.

Decomposition of benzeneazotrinitromethane in ethylcellosolve. A solution of 6.0 g of benzeneazotrinitromethane in 60 ml of ethylcellosolve was allowed to stand for 3 days at room temperature. Then the solvent was driven off, the fraction up to 115° being collected. When the latter was poured into water, an oily layer separated out; it weighed 1.5 g after separation and drying. This liquid product distilled at 75-115°, was violently decomposed by concentrated sulfuric acid, exhibited a positive reaction for nitric acid with iodine-starch paper and diphenylamine, and was completely saponified by alkali or by heating with water. All these properties indicated that the action of the liberated nitrogen oxides upon the ethylcellosolve produced nitrous acid esters. No benzene was found. The same mixture of nitrophenols, with a m.p. of 85°, was recovered from the tarry residue by extraction with hot water after the ethyl cellosolve had been driven off.

Decomposition of benzeneazotrinitromethane in carbontetrachloride with mercury present. A solution of 5.0 g of benzeneazotrinitromethane in 40 ml of carbon tetrachloride was stirred with 50 g of mercury for 3 days. At the end of the reaction, the mixture was warmed over a water bath. Nitrogen oxides were evolved. The whole reaction mass was distilled with steam. The carbon tetrachloride that distilled with the steam was separated from the water, distilled, and nitrated to remove any aromatic compounds that might have been formed from the phenyl radical. No nitro compounds were found, however. After the carbon tetrachloride had been driven off, the residue yielded a crystalline mass, which was pressed out on a porous plate and recrystallized from alcohol. This yielded 0.03 g of o-nitrophenol, with a m.p. of 44°. A sample exhibited no depression of the melting point when mixed with the pure product. The tarry product left in the flask after steam distillation was treated repeatedly with boiling water. As the aqueous extract cooled, crystals of the nitrophenols, with the same m.p. of 85°, settled out, as had been obtained in the previous experiments; they totaled 0.25 g. Salts of mercurous oxide were found in the aqueous solution. Treatment with hydrochloride acid precipitated calomel, while treatment with an alkali yielded a black precipitate (a mixture of mercury and mercurous oxide).

SUMMARY

1. Formation of the phenyl radical when benzeneazotriphenylmethane is decomposed in a carbon tetrachloride solution has been proved by the attachment of the radical to metallic mercury. Phenylmercury chloride was isolated from the solution.

2. The phenyl radical formed during the decomposition of benzeneazotriphenylmethane attaches itself to the diphenyltin added to the reaction mixture, converting the latter into hexaphenylbistannane.

3. When a solution of nitrosoacetanilide in carbon tetrachloride is heated

with diphenyltin, the latter is phenylated to tetraphenyltin.

4. When benzeneazotrinitromethane was decomposed in various organic solvents, the usual reaction products that accompany the formation of a phenyl radical: diphenyl in a benzene solution, benzene in ethylcellosolve, or diphenyl in carbon tetrachloride, were not found. Decomposing the benzeneazotrintiromethane always yielded nitrophenols, no matter what the solvent was.

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THE PHOTOREACTIONS OF ORGANOMETALLIC COMPOUNDS OF MERCURY IN SOLUTIONS

VII. THE REACTIONS OF DIPHENYLMERCURY

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In our preceding reports [1] on the photoreactions of diphenylmercury in various solvents containing a halogen, we showed that the reaction involves the formation of a phenylmercury halide and benzene whenever the solvent contains hydrogen. In the present research we have tested its photoreactions with ethyl and isopropyl bromide, β,β'-dichlorodiethyl ether (Chlorex), chlorobenzene, and bromobenzene. The reaction followed the usual course in the first three solvents: the phenylmercury radical detaching a halogen atom and being converted into a phenylmercury halide, with the phenyl radical taking up a hydrogen atom from the solvent to form benzene. Thus the elements of the hydrohalide are eliminated. We might therefore expect that gaseous (ethylene, propylene) or unsaturated products would be formed. But in none of our experiments did we find any gaseous reaction products, nor did a reaction with bromine water disclose any unsaturated compounds.

The chlorobenzene and bromobenzene reacted differently.

When a solution of diphenylmercury in chlorobenzene was irradiated, the former broke down, yielding calomel; no other individual products were detected. After the reaction we secured a tarry mass that did not crystallize after standing for a long time. The photoreaction took a different turn in bromobenzene, phenylmercury bromide being recovered, together with p-bromodiphenyl. The latter substance was obviously formed as the result of the amphoteric substitution of a phenyl radical in the bromobenzene. Another phenyl radical might act as the hydrogen acceptor:

$$2C_6H_5\cdot + C_6H_5Br \rightarrow C_6H_6 + C_6H_5C_6H_4Br.$$

Thus, the type of interaction between the radicals and aromatic solvents that has been described by Razuvaev and Petukhov in the reaction of phenylmercury hydroxide with toluene [2] may also be observed in the photo reactions of organometallic compounds of mercury of the R_2Hg type.

We are continuing our research on reactions of this kind.

We also tested diphenylmercury dissolved in carbon disulfide and carbon disulfide with sulfur, but, in spite of prolonged irradiation, all we recovered was the original substance unchanged.

EXPERIMENTAL

Reaction of diphenylmercury with ethyl bromide. A solution of 2.0 g of diphenylmercury in 10 ml of ethyl bromide was irradiated for 15 hours in a sealed quartz test tube. No gas was evolved. A precipitate of phenylmercury bromide settled to the bottom of the test tube; it was filtered out and recrystallized from benzene, yielding 1.05 g of a substance with a m.p. of 277°. A sample

1224-

exhibited no depression when mixed with pure phenylmercury bromide. The filtrate did not give a reaction for unsaturated compounds with bromine water. It was distilled, and the distillate was nitrated, yielding m-dinitrobenzene, with a m.p. of 90° (from alcohol), which exhibited no depression when mixed with the pure substance. The residue left after the solvent had been driven off was fractionally crystallized from benzene into 0.4 g of diphenylmercury (m.p. 122°) and 0.45 g of phenylmercury bromide (m.p. 277°). The total yield of phenylmercury bromide was 1.5 g (or 74% of the theoretical), 0.4 g (or 20%) of the diphenylmercury not entering into the reaction.

Reaction of diphenylmercury with isopropyl bromide. A solution of 2.0 g of diphenylmercury in 10 ml of isopropyl bromide was irradiated for 12 hours. No gas was evolved. A precipitate settled to the bottom of the test tube – phenylmercury bromide plus a minute quantity of mercury. The precipitate was filtered out, yielding 1.2 g (or 59% of the theoretical) of phenylmercury bromide, with a m.p. of 276°, which exhibited no depression when mixed with the pure substance. The filtrate was distilled, and the distillate was nitrated. This yielded m-dinitrobenzene, with a m.p. of 88-89°, which exhibited no depression when mixed with pure m-dinitrobenzene. After the solvent had been driven off, the residue yielded 0.75 g of unreacted diphenylmercury (37% of the theoretical), with a m.p. of 122°.

Reaction of diphenylmercury with Chlorex. 2.0 g of diphenylmercury was irradiated for 12 hours in 15 ml of Chlorex. The precipitate was filtered out and recrystallized from acetone. This yielded 1.25 g of phenylmercury chloride (71% of the theoretical), with a m.p. of 256°, exhibiting no depression when mixed with pure phenylmercury chloride. The filtrate was distilled, and the distillate was nitrated, yielding m-dinitrobenzene, with a m.p. of 89°.

Distillation of the residue yielded 0.1 g of unreacted diphenylmercury (5% of the sample) and 0.35 g of phenylmercury chloride, with a m.p. of 256°. The yield of phenylmercury chloride totaled 1.6 g (or 91% of the theoretical).

Reaction of diphenylmercury with benzoyl chloride. 2.0 g of diphenylmercury was irradiated for 120 hours in 15 ml of chlorobenzene. Calomel settled to the bottom of the test tube; it was filtered out and washed. The calomel totaled 1.2 g (or 92% of the theoretical). The calomel was identified by the usual reactions. The solvent was distilled from the filtrate with steam; the residue was a tarry mass, from which no individual crystalline substances could be recovered.

Reaction of diphenylmercury with bromobenzene. 1.0 g of diphenylmercury and 15 ml of bromobenzene were irradiated for 18 hours. The precipitated phenylmercury bromide was filtered out; it weighed 0.4 g, the yield of phenylmercury bromide being 40%. M.p. 275-276°, exhibiting no depression when mixed with the pure substance. The filtrate yielded 0.5 g (50% of the sample) of unreacted diphenylmercury, with a m.p. of 122°.

When we repeated this experiment, using large quantities of the original substances: 5.0 g of diphenylmercury and 25 ml of bromobenzene, and irradiating for 75 hours, we managed to secure 0.1 g of p-bromodiphenyl, with a m.p. of 89°, by distilling the filtrate with steam. A sample exhibited no depression of the melting point when mixed with pure p-bromodiphenyl.

SUMMARY

1. The photoreactions of diphenylmercury with ethyl bromide, isopropyl bromide, and Chlorex yield benzene and phenylmercury bromide or chloride.
2. When diphenylmercury is irradiated in chlorobenzene, it decomposes, yielding calomel.
3. The photoreaction of diphenylmercury with bromobenzene yields phenylmercury bromide, with p-bromodiphenyl found in the reaction products.

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*See CB translations: p.711, 1485 ff.; **713.ff.

THE ELECTROLYTIC DEHYDROGENATION OF DIETHYLACETYLENYLCARBINOL AND THE DEHYDRATION OF DIETHYLVINYLCARBINOL

A. I. Lebedeva and the Student T. A. Mishnina

The present research represents a continuation of a series of researches of the A.E.Favorsky school on the synthesis of diethylene hydrocarbons with conjugated double bonds.

The diethylene hydrocarbons are a rich field for research, in respect of the polymerizability as well.

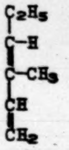
The researches of Bouchardat [1], Wallach [2], Kondakov [3], Berkengeim [4], Ostromyslensky [5], Lebedev [6], and others have established the concept that all of these hydrocarbons can be polymerized (examples are butadiene and its homologs). Subsequent research papers have dealt with efforts to explain the influence of the compound's structure upon its polymerizability (Harries [7], Macallum and Whitby [8], Fisher and Chittenden [9], and others).

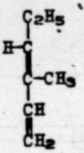
Research on the diethylene hydrocarbons is often complicated, however, by the difficulty of securing them in a sufficiently pure state and with a good yield. That is why A.E.Favorsky [10] and his pupils evolved a comparatively simple and convenient method of synthesizing dienes, starting from ketones and acetylene, via acetylene alcohols, their electrolytic hydrogenation, and the dehydration of the resultant ethylene alcohols.

Hydrogenation of acetylene alcohols to ethylene ones involves some difficulties. Some methods of hydrogenation are known, such as: in the presence of metallic sodium; with zinc dust, and acetic acid; with copperized zinc dust; and lastly, with hydrogen in the presence of nickel or palladium. Most of these methods are either expensive or inconvenient, however. Hydrogenation under pressure in the presence of nickel yields a high percentage of a saturated alcohol. The possibility of hydrogenation with the hydrogen evolved by a copper-zinc couple served as as the incentive for investigations of the electrolytic hydrogenation of acetylene alcohols. As a result of these investigations, A.E.Favorsky and A.I.Lebedeva developed a method for the electrolytic hydrogenation of acetylene alcohols; they found that when cathodes of copper and silver were used, only one molecule of hydrogen was added at the principal bond, yielding the respective ethylene alcohols.

Dimethylvinylcarbinol was secured from dimethylacetylenylcarbinol in this manner, and it was shown that dimethylacetylenylcarbinol is either not hydrogenated at all at cathodes of other metals or is hydrogenated to a saturated alcohol, amylene hydrate [12].

I.A.Shikhiev [13] hydrogenated methylpropylacetylenylcarbinol electrolytically at a copper cathode, securing methylpropylvinylcarbinol with a trace of methylethylpropylcarbinol. Dehydrating methylpropylvinylcarbinol yielded 3-methylhexadiene-1,3, apparently in two stereoisomeric forms:





The electrolytic hydrogenation of methylcyclopropylacetylenylcarbinol at a copper cathode yielded methylcyclopropylvinylcarbinol [15], it being found that the ring did not enter the hydrogenation reaction.

In the present research we had as our objective the further study of the process of electrolytic hydrogenation, inasmuch as the hydrogenation conditions may change, depending on the physical properties and structure of the various acetylene alcohols. We chose as the object of our research diethylacetylenylcarbinol, which we had synthesized by the A.E.Favorsky method [15].

The diethylacetylenylcarbinol thus synthesized formed a white precipitate with ammoniacal silver nitrate, which is typical of monosubstituted acetylenic compounds, and its physical constants agreed with those given in the literature.

The diethylacetylenylcarbinol was hydrogenated electrolytically by the A.E. Favorsky and A.I.Lebedeva method. Its insolublitiy in a 0.1% aqueous solution of alkali forced us to employ an aqueous-alcoholic solution. We selected the optimum water-alcohol ratio (3:2) for dissolving the diethylacetylenylcarbinol.

Hydrogenation was tested with copper cathodes, coated with cupric oxide, and with silvered copper cathodes. The best results, from the standpoint of high yield and purity of reaction product, were secured with the silvered cathodes, the copper cathodes being more sensitive to contamination and frequently requiring regeneration. The best way of recovering the hydrogenation products from the solution was extraction with ether, followed by saturation of the ether solution with carbon dioxide and fractionation. Hydrogenation was considered to have ended when we got a negative reaction with ammoniacal silver nitrate.

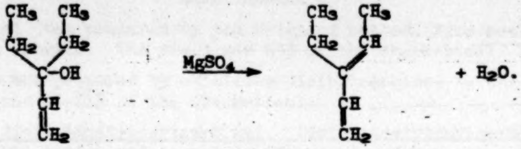
This electrolytic hydrogenation enabled us to synthesize diethylvinylcarbinol, hitherto unknown in the literature, and we determined its principal constants. Its structure was determined by catalytic hydrogenation to a saturated alcohol, triethylcarbinol, above platinum black, by bromination with a solution of bromide-bromate, and by formation of the phenylurethane, with a m.p. of 62-63°.

Hydrogenation and bromination showed that the product we had synthesized, with a b.p. of 131-133°, contained 91-97% of diethylvinylcarbinol. The impurities are due, evidently, to the presence of small amounts of water and a saturated alcohol, triethylcarbinol, as the product of a secondary process during hydrogenation.

When electrolytic hydrogenation was performed with the cathodic and anodic areas separated and at low C.D. (0.1 amp. dm^2), we expected to secure (together with the diethylvinylcarbinol at the cathode) the unknown diacetylene glycol, 3,8-diethyldecadiyne-4,6-diol-3,8 at the anode, as in the formation of dimethyloctadiynediol from dimethylacetylenylcarbinol [16]. But we got only traces of the glycol in our experiments, carried out in an aqueous-alcoholic medium. We secured a high yield of 3,8-diethyldecadiyne-4,6-diol-3,8 by the Zalkind and Aizikovich method [17], and determined its principal constants.

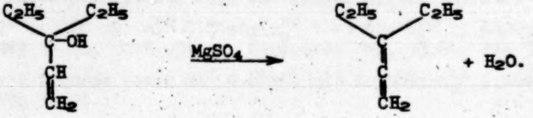
The diethylvinylcarbinol was dehydrated in a current of carbon dioxide at a at a temperature of 220-230° over calcined magnesium sulfate and at a temperature of 260-270° over small porous plates. In both instances we secured a hydrocarbon that had a very broad boiling point, 94-105°, the bulk of it boiling at 96-103° after having been desiccated and distilled over metallic sodium. We expected dehydration to yield us 3-ethylpentadiene-1,3, as follows:

1)



But it was theoretically possible to assume that the water would be split off differently, forming an allene hydrocarbon, as-diethylallene:

2)



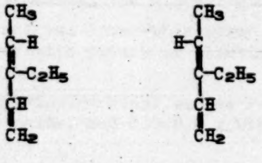
We therefore oxidized the resultant hydrocarbon with an aqueous solution of permanganate to determine its structure.

Analysis of the oxidation products disclosed traces of a carbonyl compound, apparently diethyl ketone, and a mixture of acetic and propionic acids.

The presence of traces of diethyl ketone after oxidation might be attributed to a slight contamination of the dehydration products with diethylallene, though it could also be produced by the oxidation of methyldiethylethylene (the dehydration product of the saturated alcohol, triethylcarbinol). In any event, if there was any diethylallene or methylethylethylene present in the dehydration products, the amount must have been insignificant. Inasmuch as only acetic and propionic acids were found in the oxidation products, we could assert that the hydrocarbon we had secured by dehydrating diethylvinylcarbinol was 3-ethylpentadiene-1,3. In addition to oxidation, condensation with maleic anhydride was used to confirm the structure of the 3-ethylpentadiene-1,3. It is characteristic that piperylene hydrocarbons polymerize quickly when condensed with maleic anhydride, often forming no condensates; we therefore performed the condensation in a benzene solution chilled to 0°. The bulk of the hydrocarbon was divided into two fractions, and each fraction was condensed separately with the maleic anhydride.

The first hydrocarbon fraction, with a b.p. of 96-100°, yielded a condensate with a m.p. of 71-72° (from ligroin). The second hydrocarbon fraction, with a b.p. of 100-103° likewise yielded a condensate with a m.p. of 70.5-71.5°. A mixed sample of the two condensates exhibited no depression, so that we took them to be identical.

As in the instance described above, we may assume a cis-trans isomerism here:



Dehydrating diethylvinylcarbinol yielded a small amount of a higher boiling product, in addition to the 3-ethylpentadiene-1,3. Analysis showed that this product was largely the dimer. We did not determine the structure of the dimer; it is assumed that the dimer possesses a cyclic structure.

EXPERIMENTAL

Diethylcarbinol was prepared by the Grignard method, from methyl formate and ethylmagnesium bromide. The yield was 63% of the theoretical.

Diethylketone was prepared by oxidizing diethylcarbinol by the Lieben method [18]. The yield was 60-61% of the theoretical.

Synthesis of diethylacetylenylcarbinol. Diethylacetylenylcarbinol was synthesized from diethyl ketone and acetylene with powdered potassium hydroxide, by the A.E.Favorsky method. The yield of the alcohol was 70-71%.

The carbinol is a colorless liquid with a typical turpentine odor; it yields a characteristic white precipitate with ammoniacal silver nitrate:

B.p. 136-137° at 760 mm; d_4^{20} 0.8691; n_α^{20} 1.43387; n_β^{20} 1.44225. Found: MR_α 33.88; MR_β 34.11. $C_7H_{12}OF$. Computed: MR_α 33.84; MR_β 34.58.

A.E.Favorsky's figures [15]: d_4^{17} 0.8748; n_α^{14} 1.4585; n_β^{14} 1.44697. Found: MR_α 35.58; MR_β 34.01.

A small quantity of tetraethylbutynediol was secured as a by-product of the reaction. Its yield did not exceed 7-8% of the principal reaction product. The glycol had a m.p. of 80-81° after triple recrystallization from ether.

Synthesis of diethylvinylcarbinol. The diethylacetylenylcarbinol was hydrogenated electrolytically by the A.E.Favorsky and A.I.Lebedeva method [11]. A copper plate 2.3 x 0.8 cm^2 in size served as the cathode. After the copper plate had been cleaned with emery and washed in dilute acid and in water, it was coated with cupric oxide (by heating over a soldering flame) in one series of tests, while in another series it was coated with a fine layer of silver by the method of displacement from an acidulated solution of silver nitrate (2.5 g of $AgNO_3$ and 1 ml of HNO_3 per liter of water). Then the plate was attached to the inner wall of a battery jar. A coil of nickel wire served as the anode. The anolyte was separated from the catholyte by means of a porous cylinder.

The composition of the catholyte was: 10 g of diethylacetylenylcarbinol, 0.1 g of sodium hydroxide, 100 ml of alcohol, and 150 ml of distilled water. The anolyte consisted of 100 ml of a 40% solution of sodium hydroxide. The current used was 1 ampere during the first 3 hours and 0.5 ampere thenceforth until hydrogenation was complete.

Hydrogenation was continued until the reaction for an acetylenic hydrocarbon (with ammoniacal silver nitrate) was negative. The whole run required 7.75-8 ampere-hours, or about 50% more than the theoretically calculated quantity (4.8 ampere-hours). When hydrogenation was over, the synthesized diethylvinylcarbinol usually floated on top of the electrolyte as an insoluble transparent layer. It was recovered in the pure state by extracting it with an alcoholic solution of ether, saturating the ether extract with carbon dioxide, desiccating it with calcined potash, and then fractionating the alcohol-ether mixture.

The yield of the carbinol was lower when other recovery methods were employed, such as salting out the layer with potash or diluting the catholyte to 3 or 4 times its volume with water.

The yield of the diethylvinylcarbinol was as follows: 6.0-6.5 g with copper cathodes coated with cupric oxide, and 8.0-8.2 g with silvered copper cathodes.

Diethylvinylcarbinol is a substance with a minty odor, that does not yield a precipitate with ammoniacal silver nitrate and decolorizes an aqueous solution of permanganate and bromine water in the cold.

B.p. 131-133°; d_4^{20} 0.8475; n_α^{20} 1.43185; n_β^{20} 1.44056. Found: MR_α 34.87; MR_β 35.49. $C_7H_{12}O\Gamma$. Computed: MR_α 35.38; MR_β 36.03.

Catalytic hydrogenation of diethylvinylcarbinol. Hydrogenation was carried out in the S.V.Lebedev apparatus [6]. The platinum black used was prepared by the Fokin-Willstatter method. Ether was used as the solvent.

0.5457 g substance: 0.25 g platinum black, 30 ml ether; Δt 14.1°. P 763.3 mm. Computed: 2 Hy500.2 ml. Found: 475.8 ml (454.6 ml under standard conditions); per cent ethylene alcohol: 90.9%.

Hydrogenation yielded a triethylcarbinol:

B.p. 140-141°; $d_4^{19.7}$ 0.8314; $n_\alpha^{19.7}$ 1.42047; $n_\beta^{19.7}$ 1.43090. Found: MR_α 35.60; MR_β 36.10. $C_7H_{16}O$. Computed: MR_α 35.88. MR_β 36.44.

Titration of diethylvinylcarbinol with a bromide-bromate solution.

0.1293 g substance: 0.1250 g Br. 0.1521 g substance: 0.1458 g Br. Found %: Br 96.97, 95.20.

Synthesis of the phenylurethane of diethylvinylcarbinol. The diethylvinylcarbinol was sealed into an ampoule with an equimolar quantity of phenyl isocyanate. Three months later a precipitate had formed in the ampoule. The ampoule was opened, and its contents treated with petroleum ether. The phenylurethane had a m.p. of 62-63° after recrystallization from petroleum ether.

0.2421 g substance: 12.9 ml N_2 (20°, 748 mm). 0.1040 g substance: 5.3 ml N_2 (19°, 742 mm). Found %: N 6.02, 5.79; $C_{14}H_{19}O_2N$. Computed %: N 6.00. 0.1030 g substance; 17.1 g benzene: Δt 0.132°. 0.2215 g substance: 17.1 g benzene: Δt 0.287°. Found: M 234.8, 231.1. $C_{14}H_{19}O_2$. Computed: M 233.3.

Synthesis of 3-ethylpentadiene-1,3. 28 g of diethylvinylcarbinol was passed a drop at a time for 4.5 hours in a current of CO_2, through a glass tube filled with calcined magnesium sulfate (in other tests the tube was filled with small porous plates) that was placed in a tubular furnace set up at a slant and heated to 220-230°. The dehydration product was collected in a receiver externally chilled with ice. It was a slightly greenish, mobile liquid, with an acrid odor. After dehydration was complete, the hydrocarbon was separated from the water, desiccated with potash, and distilled. The crude hydrocarbon weighed 22 g.

After the major fraction (b.p. 96-105°) had been distilled, there remained in the flask a certain quantity of condensation products that could not be distilled at ordinary pressure. The bulk of the hydrocarbon was again desiccated with $CaCl_2$ and redistilled above metallic sodium.

Two fractions were collected:

I 96-100°, 6.7 g; II 100-103°, 5.7 g.

Analysis of Fraction I, with a b.p. of 96-100°: d_4^{20} 0.7505; d_4^0 0.7681; n_α^{20} 1.43882; n_β^{20} 1.45242; Found: MR_α 33.63; MR_β 34.80. $C_7H_{12}\Gamma_2$. Computed: MR_α 33.372; MR_β 34.80.

Three grams of 3-ethylpentadiene-1,3 was condensed with 3 g of maleic anhydride in a benzene solution chilled to 0°. The mixture was sealed in an ampoule and kept at 0° for 4 days. Then the benzene was driven off in vacuum and the precipitate was processed with hot ligroin (b.p. 87-97°). The cubic crystals that settled out of the solution were recrystallized four times from ligroin; their m.p. was 71-72° after desiccation in a vacuum desiccator.

Analysis of the condensate of 3-ethylpentadiene-1,3 and maleic anhydride (1-methyl-2-ethyltetrahydrophthalic anhydride-5,6): 0.0943 g substance: 0.2360 g CO_2; 0.0632 g H_2O. 0.1069 g substance: 0.2666 g CO_2; 0.0691 g H_2O. Found %: C 68.25, 68.07; H 7.49, 7.23. $C_{11}H_{14}O_3$. Computed %: C 68.02; H 7.26. 0.1591 g substance: benzene 17.02 g: Δt 0.245°. 0.3395 g substance: benzene 17.02 g: Δt 0.510°. Found: M 195.73, 200.64. $C_{11}H_{14}O_3$. Computed M 194.22.

Analysis of Fraction II of the hydrocarbon, with a b.p. of 100-103°: d_4^{20} 0.7473; n_α^{20}1.44638. Found: MR_α 34.27: $C_7H_{12}\digamma_2$. Computed: MR_β 33.372.

The condensate with maleic anhydride was prepared under the same conditions as used for Fraction I. M.p. 70.5-71.5°. A mixed sample of the condensates of both fractions had a m.p. of 70.5-71.5°.

Determination of the Structure of the Dehydration Product (of 3-Ethylpentadiene-1,3) By Oxidation with an Aqueous Solution of Permanganate

We used 5 g of the hydrocarbon with a b.p. of 96-103° in this oxidation. On the basis of the oxidation of 2 double bonds, we weighed out 49 g of permanganate, part of which was dissolved in 400 ml of water, the other part being added as a powder. 42 g of the permanganate was used up. After the manganese dioxide had been filtered out of the solution, the neutral products were driven off. The first runnings of the distillate contained traces of a ketone, p-nitrophenylhydrazone, with a m.p. of 129-130°. We were unable to purify the synthesized paranitrophenylhydrazone by recrystallization because of the minute quantity recovered.

After the neutral products had been driven off, the solution was concentrated by evaporating it over a water bath, acidulated with dilute sulfuric acid, and then distilled to isolate the volatile acids. The bulk of the distillate was processed by heating it with freshly precipitated silver carbonate over a water bath; the silver salt in the solution was freed from the residue of silver carbonate by filtration and then fractionally crystallized.

Analysis of the various fractions for their silver content yielded the following results:

Fraction I 0.0605 g salt: 0.0362 g Ag; 59.83% Ag. Fraction II 0.1171 g salt: 0.0709 g Ag; 60.55% Ag. Fraction III 0.0802 g salt: 0.0491 g Ag; 61.22% Ag. Fraction 4 0.2315 g salt: 0.1428 g Ag; 61.68% Ag. Fraction V 0.1943 g salt: 0.1223 g Ag; 62.94% Ag. Fraction VI 0.1030 g salt: 0.0654 g Ag; 63.49% Ag. $C_3H_5O_2Ag$. Computed %: Ag 59.66. $C_2H_3O_2Ag$. Computed %: Ag 64.67.

The residue left after the volatile acids had been driven off was extracted with ether in an extractor. No nonvolatile acids were detected after the ether had been driven off.

These findings indicate that the oxidation products were acetic and propionic acids (the propionic acid was apparently formed as the result of further oxidation of β-methylpyruvic acid), plus traces of diethyl ketone. Hence, the hydrocarbon under test had the structure of 3-ethylpentadiene-1,3.

When we analyzed the neutral products of ozonolysis after the 3-ethylpentadiene-1,3 had been ozonated, we again found only traces of the p-nitrophenylhydrazone.

Analysis of the Dimer

When we dehydrated the diethylvinylcarbinol, we secured, in addition to the monomer, a small quantity of a rather viscous yellow liquid, which was distilled in vacuum, the following fractions being collected:

I 104-110° (10 mm); II 110-130° (10 mm); III 130-150° (8 mm).

Analysis of Fraction I:

d_4^{21} 0.8380; n_α^{21} 1.47002. Found: MR_α 63.94. $C_{14}H_{24}\Gamma^{=}_2$. Computed: MR_α 63.362. 0.1101 g substance: 17.50 g benzene: Δt 0.180°. Found: M 179.3. $C_{14}H_{24}$. Computed: M 192.3.

Analysis of Fraction II.

$d_4^{21.5}$ 0.8866; $n_\alpha^{21.5}$ 1.46982. Found: MR_α 63.86. $C_{14}H_{24}\Gamma^{=}_2$. Computed: MR_α 63.362. 0.1799 g substance; 20.00 g benzene: Δt 0.230°. Found: M 200.6. $C_{14}H_{24}$. Computed: M 192.3.

Analysis of Fraction III.

$d_4^{21.5}$ 0.8866; $n_\alpha^{21.5}$ 1.48958. Found: MR_α 63.78. $C_{14}H_{24}\Gamma^{=}_2$. Computed: MR_α 63.362. 0.2937 g substance: 15.91 g benzene: Δt 0.343°. Found: M 260.0. $C_{14}H_{24}$. Computed: M 192.3.

The analyses of Fraction I and II indicate the presence of a dimer, most likely of cyclic structure. We have been unable to determine the structure of this dimer as yet, owing to the fact that the quantity available has been too small.

Synthesis of 3,8-Diethyldecadiyne-4,6-diol-3,8

Ten g of cuprous chloride and 10 g of diethylacetylenylcarbinol were added to 30 g of ammonium chloride dissolved in 100 ml of water. The solution was agitated for 15-20 minutes, poured into a large porcelain dish, and set aside to stand until the following day. The precipitate was then suction-filtered. This operation was repeated as long as crystals continued to settle out. Recrystallization from benzene yielded 6.5 g of the glycol (65% of the theoretical) with a m.p. of 113-114°

0.1163 g substance: 0.3231 g CO_2; 0.1046 g H_2O. 0.1155 g substance: 0.3213 g CO_2; 0.1016 g H_2O. Found %: C 75.76, 75.86. H 10.01, 9.84. $C_{14}H_{22}O_2$. Computed %: C 75.63; H 9.97. 0.1358 g substance; 22 g benzene Δt 0.142°. 0.1057 g substance: 22 g benzene: Δt 0.112°. Found: M 222.9, 223.8. $C_{14}H_{22}O_2$. Computed: M 222.3.

SUMMARY

1. A study has been made of the electrolytic hydrogenation of diethylacetylenylcarbinol to diethylvinylcarbinol, and the optimum conditions for hydrogenation have been found to be a silvered copper electrode in an aqueous-alcoholic alkaline electrolyte.

2. The hitherto unknown diethylvinylcarbinol has been synthesized by electrolytically hydrogenating diethylacetylenylcarbinol, and the new carbinol has been characterized.

3. Dehydrating diethylvinylcarbinol has yielded an hitherto unknown hydrocarbon, 3-ethylpentadiene-1,3, which has been characterized, plus the dimer of this hydrocarbon.

4. The condensate of 3-ethylpentadiene-1,3 with maleic anhydride has been synthesized.

5. The hitherto unknown diacetylenic glycol 3,8-diethyldecadiyne-4,6-diol-3,8 has been synthesized.

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RESEARCH ON THE ISOMERIZATION AND POLYMERIZATION OF DIMETHYLVINYLCARBINOL AS FUNCTIONS OF THE REAGENT pH

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When dilute sulfuric acid was reacted with dimethylvinylcarbinol [1], we secured a complex mixture of products, from which we isolated isoprene, the initial carbinol, γ ,γ-dimethylallyl alcohol, α,α-dimethylene glycol, linalool, geraniol, and terpin hydrate, and in which it was assumed that nerolidol and farnesol were present. The same complex mixture was secured when we reacted sulfuric acid with isoprene in acetic acid [2]. But in all our previous research all we did was to isolate and identify the products without investigating the effect of various factors upon the reaction with a view to turning the reaction into the channel of the formation of terpene alcohols, which are extensively employed in the perfume industry. Since dimethylvinylcarbinol is relatively accessible, acetylene could then be used as a base for the synthesis of fixatives and bases for scents in the perfume industry. We therefore set as our objective in the present research a study of the transformations of dimethylvinylcarbinol as they are affected by the hydrogen-ion concentration (pH) of the reagent and, in part, by the temperature.

Besides the aqueous and aqueous-alcoholic solutions of sulfuric acid, we decided to explore the action of aqueous solutions of acid sulfates and phosphates and aqueous solutions of hydrochloric acid. No one had as yet done any research on the action of acid sulfates and phosphates upon dimethylvinylcarbinol.

I.N.Nazarov and I.N.Azerbaev [3] investigated the action of hydrogen chloride upon dimethylvinylcarbinol and secured two isomeric chlorides: α,α-dimethyl allyl chloride and γ,γ-dimethyl allyl chloride; they do not say, however, whether they obtained high-boiling terpene fractions or investigated them.

In our research we used aqueous and, in some instances, aqueous-alcoholic solutions of disodium phosphate, monosodium phosphate, potassium bisulfate, and solutions of sulfuric and hydrochloric acids of various concentrations. We measured the hydrogen-ion concentration of these solutions and then tested the action of the solutions upon dimethylvinylcarbinol, using a fixed ratio of the dimethylvinylcarbinol to the reagent (1:3 or 1:1).

The emf of the solutions was measured potentiometrically with a glass electrode. The solution pH was calculated from the emf. The tests of disodium phosphate and monosodium phosphate were run at room temperature (agitating the mixture for 30 hours) as well as by heating the mixture for 8 hours over a water bath.

The tests of sulfuric acid, potassium bisulfate, and hydrochloric acid were run at room temperature (agitation for 30 hours). 70 g of dimethylcarbinol (100 g of the commercial product) was used in each test. Our results are listed in Table 1.

The per cent of the terpene fractions was based on the reacted dimethyl-

TABLE 1

Test No.	Reagent	pH of reagent	Reaction conditions	Yield of terpene and sesquiterpene fractions		Remarks
				g	%	
1	10% Na_2HPO_4	8.74	Room temperature	–	–	
2		8.74	Heated over a water bath	–	–	
3	10% NaH_2PO_4	4.42	Room temperature	–	–	
4		4.42	Heated over a water bath	–	–	
5	0.1 $\underline{N}$ H_2SO_4	1.32	Room temperature	–	–	Aqueous-alcoholic solution water: alcohol ratio = 1:1
6	0.1 N H_2SO_4	1.29	Room temperature	–	–	Formation of an alcohol via allyl rearrangement is observed
7	0.25 N H_2SO_4	1.27	Room temperature	1.0	2.8	
8	10% $KHSO_4$	1.25	Room temperature	1.8	5.6	
13	1% HCl	1.18	Room temperature	2.9	6.8	
14	5% HCl	0.95	Room temperature	8.1	13.7	

vinylcarbinol. We see in Table 1 that the yield of terpene fractions is directly related to the pH of the reagent. At pH values ranging from 9 to 1.3 the reagent does not affect the dimethylvinylcarbinol at all, the latter being recovered unchanged (cf Tests 1-5). Isomerization is observed at a pH below 1.3 (cf Test 6). At still higher hydrogen-ion concentrations in the reagent, the latter's polymerizing, or rather dimerizing, action is intensified, and fractions corresponding to the terpene alcohols appear (cf Test 7 et seq.).

As the hydrogen-ion concentration rises, the yield of dimers and trimers, corresponding to the terpene and sesquiterpene alcohols, rises in parallel. In order to calculate the effect of temperature upon the reaction, we took a 10% aqueous solution of potassium bisulfate, which had a pH of 1.25, and tested the action of this solution at room temperature, at the temperature of a boiling water bath, and at 130-140° (in a sealed tube), the proportions of the dimethylvinylcarbinol and the solution used being 1:3 in the first two tests and 1:1 in the last three. The results of these tests are listed in Table 2.

The figures in Table 2 indicate that the highest yield of the terpene and sesquiterpene fractions (18.5%) was observed in Test 10, when the 1:1 mixture of dimethylvinylcarbinol and a 10% aqueous solution of potassium bisulfate was heated for 8 hours over a water bath with a reflux condenser. Tests 11 and 12 were run under the same conditions as Test 10, but in sealed tubes.

We see from Table 2 that raising the reaction temperature or the heating time does not increase the yield of the terpene fractions.

We investigated the products obtained in the various mixtures as follows. After appropriate processing, the upper layer of the mixture was separated from the lower one, washed with an aqueous solution of soda, desiccated, and distilled. The lower, aqueous layer was extracted with ether in a percolator, washed, desiccated, and distilled.

TABLE 2

Test No.	Reaction conditions	Yield of terpene and sesquiterpene fractions		Remarks
		grams	per cent	
8	15-18° (30 hours)	1.8	5.6	
9	95-98° (8 hours)	7.6	11.6	
10	95-98° (8 hours)	10.7	18.5	
11	95-98° (16 hours)	4.2	9.1	In sealed tubes
12	130-140° (8 hours)	7.3	11.0	

More or less constant fractions, boiling in the following ranges, were secured from the upper layer:

I 33-34°; II 80-102°; III 140-142°; IV 86-89° (9 mm);
V 107-110° (9 mm); VI 136-140° (9 mm); VII 159-161° (9 mm).

Fraction I turned out to be isoprene; it was characterized by condensing it with maleic anhydride. The condensate had a m.p. of 63-63.5°. Moreover, the isoprene was hydrogenated catalytically with platinum black and oxidized with permanganate. Hydrogenation and oxidation demonstrated that the isoprene contained a trace of an ethylenic hydrocarbon, apparently trimethylethylene, produced by dehydration of the dimethylvinylcarbinol. The physical constants of Fraction II were those of the initial dimethylvinylcarbinol, while Fraction III's constants were those of the isomeric γ,γ-dimethyl allyl alcohol. Fractions IV and V were secured in the pure state after repeated distillation in an atmosphere of carbon dioxide; they were characterized by their correspondence with the data in the literature. Fraction IV was linalool, and V was geraniol. It was very difficult to isolate Fractions VI and VII in the pure state. Their boiling points and molecular weights indicated that they were nerolidol and farnesol, respectively; but when we determined their hydroxyl content by the Terentyev-Shcherbakov method, their specific gravity, and their molar refraction, the results were conflicting. When we oxidized these fractions with chromic acid by the method recommended by Ruzicka [4] in order to produce farnesal, we secured a product that formed a silver mirror but did not yield crystalline derivatives with semicarbazide or p-nitrophenylhydrazine. Kerschbaum affirms [5] that synthetic farnesal does not form a semicarbazone.

The ether was driven out of the lower, aqueous layer, yielding the initial dimethylvinylcarbinol, γ,γ-dimethyl allyl alcohol, α,α-dimethyl trimethylene glycol, characterized by its monophenylurethane with a m.p. of 88-89°, and terpin hydrate, with a m.p. of 116-116.5° (from water), which exhibited no depression when mixed with known terpin hydrate. The α,α-dimethyl trimethylene glycol and the terpin hydrate were found in the lower layer in the tests using potassium bisulfate and 5% hydrochloric acid.

A substance that distilled at 105-112° (12 mm) was extracted from the lower layer obtained from the sealed tubes (Tests 11 and 12). The analytical data (with the exception of the molecular weight) indicated that this compound was terpin hydrate, while its molecular weight was that of terpin; we were unable to secure it in crystalline form.

Thus the whole series of substances found by A.E.Favorsky and A.I.Lebedeva [1] when they reacted 30% sulfuric acid with dimethylvinylcarbinol, was isolated and characterized in our experiment, using a 10% solution of potassium bisulfate and 5% hydrochloric acid (Tests 10 and 14). The fraction whose boiling point was that of farnesol was secured only with 5% hydrochloric acid at room temperature.

The Beilstein test for chlorine was negative in all the higher fractions in the mixture. Some of the lower fractions contained chlorine, but they were not analyzed further. All the products isolated served to confirm the fact that under our experimental conditions, we observed step-by-step polymerization in addition to isomerization, dehydration, and hydration, the polymerization chain being broken off at the stage in which dimers and trimers that contained hydroxyl groups were formed.

Practically no rubbery polymers were observed in any of the tests.

EXPERIMENTAL

The initial commercial product boiled at 85-98° and contained 70.2% dimethylvinylcarbinol (determined by titration with bromide-bromate).

In each test we took 100 g of the commercial dimethylvinylcarbinol and 100 or 300 ml of the respective aqueous solution. In the tests run at room temperature the mixture was placed in a bottle with a ground-glass stopper and shaken for 30 hours. In the tests in which heat was applied, the mixture was placed in a flask fitted with a reflux condenser, or in an ampoule, and heated for the required length of time. Then the layers were separated, the upper one being washed with an aqueous solution of soda, desiccated with calcined potash, and distilled. The lower layer was extracted for a long time with ether in a percolator, and the ether extract was washed with an aqueous solution of soda and desiccated with calcinced potash. Then the ether was driven off, and the product was distilled. The high-boiling fractions were distilled in a current of carbon dioxide. The conditinns used in all the tests and the yields of the principal reaction products are tabulated in Table 3.

I. Analysis of the Fractions Secured from the Upper Layer

All of the most characteristic fractions were identified separately in each test; we used only the data of a single analysis for each fraction in our research, however.

1. Fraction with a b.p. of 33-40°.

This fraction yielded a substance with a b.p. of 33-34°. One gram of the substance was heated with 1.3 g of maleic anhydride in a sealed ampoule for 4 hours over a water bath. The precipitated crystals were recrystallized from ligroin, after which they had a m.p. of 63-63.5°, which is the melting point of the condensate of isoprene with maleic anhydride.

Oxidation of Fraction I with an aqueous permanganate solution. We used 5 g of the fraction and 70 g of permanganate for this oxidation. Only 64.3 g of the permanganate entered into the oxidation reaction in aqueous solution in the cold.

The manganese dioxide was suction-filtered out, and acetone was distilled from the remaining neutral products, yielding a precipitate of its p-nitrophenylhydrazone with a m.p. of 147.5°. A fusion sample exhibited no depression when mixed with the known p-nitrophenylhydrazone of acetone. Acetone could be formed only by the oxidation of trimethylethylene, secured by the dehydration of dimethylethylcarbinol, present as an impurity in the original dimethylvinylcarbinol. Formic acid, which displayed a positive qualitative reaction with Kucherov's reagent, was distilled from the acidulated solution. The only way for the formic acid to be formed was by the oxidation of isoprene.

Catalytic hydrogenation of the fraction with a b.p. of 33-34°. Hydrogenation was carried out in a S.V.Lebedev apparatus [6], using 0.5 g of platinum black, 40 ml of absolute alcohol and 1.3 g of the substance under test. Theoretically, 832 ml of H_2 should have been added; actually 650 ml were (78% of the theoretical).

2. Fraction with a b.p. of 80-102°.

This fraction yielded a substance with a b.p. of 96-98°.

$n_{\alpha}^{17.3}$ 1.41168; $d_4^{17.3}$ 0.8255. Found: MR_{α} 25.92. $C_5H_{10}O\Gamma$. Computed: MR_{α} 26.193.

These figures agree with those for the initial dimethylvinylcarbinol.

3. Fraction with a b.p. of 135-142°.

This fraction yielded a substance with a b.p. of 140-142°.

n_{α}^{21} 1.44154; d_4^{21} 0.8540. Found: MR_{α} 26.62. $C_5H_{10}O\Gamma$. Computed: MR_{α} 26.193.

These figures agree with those for primary γ,γ-dimethyl allyl alcohol.

4. Fraction with a b.p. of 86-89° (9 mm).

n_{α}^{23} 1.44653; d_4^{2} 0.8433. Found: MR_{α} 48.76. $C_{10}H_{18}O\Gamma_2$. Computed: MR_{α} 48.680. 0.2045 g substance; 20.60 g benzene: Δt 0.330°. 0.2793 g substance; 17.9 g benzene: Δt 0.510°. Found: M 154.1, 156.9. $C_{10}H_{18}O$. Computed: M 154.14. 0.0961 g substance: 0.2736 g CO_2; 0.1016 g H_2O. 0.0727 g substance. 0.2074 g CO_2; 0.0768 g H_2O. Found %: C 77.65, 77.79; H 11.83, 11.82. $C_{10}H_{18}O$. Computed %: C 77.93; H 11.69.

These figures agree with those for linalool.

5. Fraction with a b.p. of 90-107° (9 mm).

According to Lennartz [2], this fraction contained two primary aliphatic terpene alcohols (with b.p. of 95-97° at 14 mm and 100-103° at 14 mm) that had the odor of lavender and were isomeric with linalool. Lennartz did not establish the structure of these alcohols. We did not separate these alcohols, but analyzed the mixture.

n_{α}^{22} 1.45114; d_4^{22} 0.8540; n_D^{22} 1.4560. Found: MR_{α} 48.56; MR_D 49.01. $C_{10}H_{18}O\Gamma_2$. Computed: MR_{α} 48.68; MR_D 48.97. 0.1508 g substance; 18.16 g benzene: Δt 0.275°. Found M 154.9. $C_{10}H_{18}O$. Computed: M 154.14.

6. Fraction with a b.p. of 107-110° (9 mm).

n_{α}^{22} 1.45360; d_4^{22} 0.8873; n_D^{22} 1.4680. Found: MR_{α} 48.98; MR_D 48.30. $C_{10}H_{18}O\Gamma_2$. Computed: MR_{α} 48.68; MR_D 48.97. 0.1076 g substance; 17.00 g benzene: Δt 0.202°. Found: M 157.8. $C_{10}H_{18}O$. Computed: M 154.14. 0.0753 g substance; 0.2142 g CO_2; 0.0780 g H_2O. 0.0748 g substance: 0.2135 g CO_2; 0.0786 g H_2O. Found %: C 77.58, 77.84; H 11.59, 11.76. $C_{10}H_{18}O$. Computed %: C 77.93; H 11.69.

The foregoing data indicate that this fraction consisted of geraniol.

7. Fraction with a b.p. of 136-140° (9 mm).

n_{α}^{21} 1.46376; d_4^{21} 0.9262; n_{β}^{21} 1.47319. 0.1400 g substance; 17.77 g benzene: Δt 0.180°. Found: M 224.5. $C_{15}H_{26}O$. Computed: M 222.0.

The fraction with a b.p. of 136-140° (9 mm) was oxidized with a chromic acid mixture by Ruzicka's method [4]. 5.6 g of the substance was dissolved in 14 ml of glacial acetic acid. To this solution we added 5.6 g of potassium bichromate in 125 ml of water and 7 g of sulfuric acid (sp. gr. 1.84). The solution turned green after 20 minutes of heating to 60-80° over a water bath, giving off a strong lemon odor. The solution was extracted with ether. The ether extract was washed with a dilute alkali solution and desiccated with calcined potash; driving off the ether then left behind an oil that distilled at 119-120° (2 mm). It formed a silver mirror with ammoniacal silver nitrate, but did not react with semicarbazide

TABLE 3

Test No.	Reagent	Ml of reagent	Test Temp. (°)	Processing time, hrs.	G. of unreacted dimethylvinylcarbinol (b.p. 80-103° rec. after react.	Yield of reaction products (g)			Remarks
						Isoprene (b.p. 33-40°)	γ,γ-dimethyl allyl alcohol (b.p. 135-142°)	Terpene fractions (b.p. 85-160°, 9mm)	
1	10% N_2HPO_4	100	15-18	30	68.8	–	–	–	
2		100	95-98	8	62.5	–	–	–	
3	10% NaH_2PO_4	100	15-18	30	67.0	–	–	–	
4		100	95-98	8	63.0	–	–	–	
5	0.1 N H_2SO_4	300	15-18	30	68.0	–	–	–	Aqueous-alcoholic solution of sulfuric acid (1:1)
6	0.1 N H_2SO_4	300	15-18	30	22.1	–	4.9	–	
7	0.25 N H_2SO_4	300	15-18	30	35.0	3.3	3.7	1.0	
8	10% $KHSO_4$	300	15-18	30	37.8	0.2	5.8	1.8	
9		300	95-98	8	4.5	6.8	1.3	7.6	
10		100	95-98	8	10.0	17.4	0.4	10.7	1.2 g of a substance with b.p. 199-203° (α,α-dimethyl trimethylene glycol) recovered from the lower layer
11		100	95-98	16	23.6	5.0	5.4	4.2	In a sealed tube 2.1 g of a substance with b.p. 105-112° (12 mm) recovered from the lower layer
12		100	130-140	8	4.0	12.0	3.3	7.3	In a sealed tube
13	1% HCl	300	15-18	30	27.4	0.1	0.8	2.9	
14	5% HCl	300	15-18	30	8.7	4.0	3.6	8.1	4.8 g of a substance with b.p. of 106-145° (20 mm) recovered from the lower layer

or p-nitrophenylhydrazine. Hence, the presence of nerolidol in this fraction has not been proved conclusively.

8. Fraction with a b.p. of 159-161° (9 mm).

This fraction was secured only when the dimethylvinylcarbinol was reacted with 5% hydrochloric acid at room temperature.

n_{α}^{19} 1.46854; d_4^{19} 0.9376; 0.1587 g substance; 18.36 g benzene: Δt 0.195°.
Found: M 227.3. $C_{15}H_{26}O$. Computed: M 222.0.

This fraction was not analyzed any further.

II. Analysis of the Fractions Secured from the Lower Layer

1. Fraction with a b.p. of 103-104° (13 mm); 106-110° (20 mm); 199-203° (760 mm).

n_{α}^{20} 1.44913; d_4^{20} 0.9683; Found: MR_{α} 28.8. $C_5H_{12}O_2$. Computed: MR_{α} 28.2. 0.2032 g substance; 18.20 g benzene: Δt 0.541°. Found: M 105.7. $C_5H_{12}O_2$. Computed: M 104.0.

A monophenylurethane was prepared from 1 g of the fraction and 1 g of phenyl isocyanate. The phenylurethane precipitate was thrown down very quickly when the two solutions were combined. The crystals (from alcohol) had a m.p. of 88-89°. A fusion sample exhibited no depression when mixed with the known monophenylurethane of α,α-dimethyl trimethylene glycol (m.p. 88-89°).

2. Fraction with a b.p. of 127-145° (20 mm).

After this fraction had been allowed to stand for 4 days, white crystals that had a m.p. of 116-116.5° (from water) settled out. A fusion sample exhibited no depression when mixed with known terpin hydrate.

3. Fraction with a b.p. of 105-112° (12 mm).

When the products obtained by extracting the lower layer with ether were distilled, we secured a substance with the odor of pine needles in the tests in which sealed ampoules were used. This substance distilled within the temperature range indicated above and was analyzed as follows:

n_{α}^{19} 1.44412; d_4^{19} 0.9628. Found: MR_{α} 52.43. $C_{10}H_{22}O_3$. Computed: MR_{α} 52.720. 0.1435 g substance; 16.75 g benzene: Δt 0.255°. Found: M 174.0. $C_{10}H_{20}O_2$. Computed: M 172.16. $C_{10}H_{23}O_3$. Computed: M 190.17. 0.0892 g substance: 0.2074 g CO_2; 0.0883 g H_2O. 0.1271 g substance: 0.2955 g CO_2; 0.1354 g H_2O. Found %: C 63.41, 63.40; H 11.07, 11.90. $C_{10}H_{23}O_3$. Computed %: C 63.10; H 11.66.

These data are those of terpin hydrate; we were unable to secure the compound in crystalline form, however.

SUMMARY

1. It has been found that the yield of terpene products varies with the pH of the reagent when dimethylvinylcarbinol is reacted with acid reagents.

2. A definite reagent pH, not exceeding 1.3, is required for the formation of terpenes from dimethylvinylcarbinol.

3. The parallel reactions of hydration, dehydration, isomerization, and polymerization may be effected by hydrochloric acid and acid sulfates, as well as by sulfuric acid, i.e., by all compounds that furnish given hydrogen-ion concentration.

4. At a given solution pH of 1.25, the optimum yield of terpenes and sesquiterpenes is obtained with heating a 1:1 mixture over a water bath.

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Chair of the Structure of Organic
Compounds
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SYNTHESES OF DERIVATIVES OF α-AMINO ACIDS

I. N$^{\alpha}$-BENZENESULFO SUBSTITUTED DERIVATIVES OF l- AND d-LYSINE

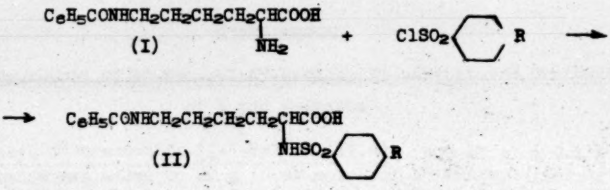
V. F. Kucherov and A. I. Ivanov

Of the various derivatives of substances that are important biologically, the derivatives of the α-amino acids are of considerable interest, since these derivatives are important in the study of many metabolic processes. On the other hand, several derivatives of the α-amino acids have been investigated with respect to their therapeutic activity. This is true chiefly of the sulfanilamide derivatives of α-amino acids. Several examples of these compounds, containing an aminoacid residue in the sulfamide group and synthesized by condensing p-acetylaminobenzene sulfochloride with α-amino acids, have been investigated: glycine, alanine, thyrosine, and glutamic acid [1]. The simplest representative of this group – sulfanilylglycine – has attracted the greatest attention, and it has been the subject of detailed investigations.

It was found [2] that sulfanilylglycine possesses an activity toward certain cocci infections that is not inferior to that of sulfanilamide itself, and might even possess some advantage over the latter in that its water-soluble salts may be secured. Nonetheless, the number of known sulfanilamide derivatives of α-amino acids is extremely limited.

The great importance of an amino acid like lysine, which is indispensable to growth and is so important in metabolism processes, and whose derivatives exert a specific action upon metabolism [3], led us to synthesize several of its derivatives, especially N$^{\alpha}$-sulfanilyl-l- and d-lysine, together with some of the simplest sulfobenzene-substituted derivatives of l- and d-lysine.

We did this by condensing N$^{\epsilon}$-benzoyllysines (I) with several sulfochlorides in an alkaline medium in a Schotten-Baumann reaction, as described for the simplest case, with benzene sulfochloride [4], as follows:



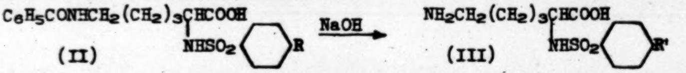
(I)

(II)

II, a R = H;
II, b R = CH_3;
II, c R = $NHCOCH_3$;
II, d R = $NHCOOCH_3$.

Similar N$^{\varepsilon}$-benzoyl- and N$^{\alpha}$-benzoylsulfo-substituted derivatives of lysine (II) were synthesized for both of the optical forms of N$^{\varepsilon}$-benzoyllysine. All of these substances are slightly soluble in water and insoluble in ether, acetone, ethyl acetate, or chloroform, and crystallize as minute colorless needles from aqueous alcohol.

The N$^{\varepsilon}$-benzoyl-l(+)-lysine required for the syntheses was prepared by hydrolyzing casein by the A.Kurtz method [5]. The N$^{\varepsilon}$-benzoyl-d(−)-lysine was synthesized by a Walden inversion from N$^{\varepsilon}$-benzyl-l(+)-lysine [6]. This method is much more convenient that separating d,l-lysine via the camphorates [7]. Saponifying the synthesized N$^{\varepsilon}$-benzoyl derivatives in alkaline solution readily yields the corresponding N$^{\alpha}$-benzenesulfo-substituted derivatives of lysine (III), as follows:



III, a R' = H;
III, b R' = CH_3;
III, c R' = NH_2.

The same result may be secured with acid saponification; the saponification conditions have to be much more severe when that is done, however. A study of the conditions governing the saponification of N$^{\varepsilon}$-benzoyl-N$^{\alpha}$-benzenesulfo-substituted derivatives of lysine shows that the sulfamide bond is much stronger than the benzoyl bond, so that we can invariably secure saponification products fairly easily and with a high degree of purity. Even 40 hours of heating with a normal NaOH solution does not result in the saponification of the sulfamide bond, nor is any racemization observed.

In the saponification of the compounds (II,c) and (II,d) the acetyl and urethylan groups are split off together with the benzoyl radical, which results in the formation of N$^{\alpha}$-(p-aminobenzenesulfanil)-lysines (III,c). Efforts to secure the intermediate products of a less thorough saponification met with failure. The saponifying time required for the production of N$^{\alpha}$-(p-aminobenzosulfanil)-lysines can be shortened to 10-15 hours. All the derivatives were secured for both optical forms of lysine.

The specific rotatory power of all the synthesized derivatives of lysine was checked. It was found that the rotatory power of all these derivatives in alkaline solutions is opposite in sign to that of the respective initial N$^{\varepsilon}$-benzoyllysine, the magnitude of the rotation varying with the concentration of the alkali.

EXPERIMENTAL

I. Synthesis of N$^{\varepsilon}$-Benzoyl-N$^{\alpha}$-benzosulfo-substituted Derivatives of l and d-Lysine

1) N$^{\varepsilon}$-Benzoyl-N$^{\alpha}$-benzosulfo-l(+)-lysine (II,a). 400 ml of a 0.1 N solution of sodium hydroxide was added to 20 g (0.08 mole) of N$^{\varepsilon}$-benzoyl-l(+)-lysine, and 42 g (0.24 mole) of pure benzene sulfochloride and 960 ml of 0.5 N sodium hydroxide solution were added simultaneously, with stirring, during the course of 30-40 minutes, at a temperature of 15-20°. The solution was stirred for 4 hours and then filtered, the filtrate being gradually acidulated with concentrated hydrochloric acid against Congo red, with vigorous stirring. When these specifications are complied with the reaction product is secured forthwith in the solid state.

The precipitate was filtered out, washed with cold water, and dried.

A single recrystallization from 50% alcohol yielded 24.4 g (78% of the theoretical) of a substance with a m.p. of 164-165°, which is in conformity with the figure in the literature [4].

2. N^{ε}-Benzoyl-N^{α}-benzosulfo-d-(-)-lysine. 15.6 g of a substance with a m.p. of 164.5-165° was secured from 12 g of N^{ε}-benzoyl-d(-)-lysine by a process like that above. Yield: 83%. The melting point remained the same after crystallization from 50% alcohol.

$[\alpha]^{20}_{D}$ + 27.6° (0.2280 g substance in 10 ml 0.5 N NaOH; l 1 dm; α +0.63°).
0.1338 g substance: 6.51 ml 0.1 N HCl. Found %: N 6.81.
$C_{19}H_{22}O_5N_2S$. Computed %: N 7.18.

3) N^{ε}-Benzoyl-N^{α}-p-toluenesulfo-l(+)-lysine (II, b). 400 ml of 0.1 N sodium hydroxide was added to 20 g (0.08 mole) of N^{ε}-benzoyl-l-(+)-lysine, and 30.6 g (0.16 mole) of distilled p-toluene sulforchloride and 605 ml of 0.5 N sodium hydroxide solution were added simultaneously, during the course of 30-40 minutes, with constant stirring. The reaction mixture was stirred for 4 hours, after which it was processed as described above for the synthesis of the benzenesulfo derivative. The synthesized crude reaction product had a m.p. of 170-171°. Recrystallization from 60% alcohol yielded 25.3 g (79% of the theoretical) of a substance in the shape of minute colorless needles with a constant m.p. of 171-172°.

$[\alpha]^{15}_{D}$ -11.6° (0.1120 g substance in 10 ml of 0.1 N NaOH); l 1 dm; α -0.13°.
$[\alpha]^{20}_{D}$ -28.6° (0.4010 g substance in 10 ml 0.5 N NaOH; l 1 dm; α -1.15°).
0.1084 g substance: 7.0 ml N_2 (23°, 744 mm). 0.1320 g substance: 0.0784 g $BaSO_4$. Found %: N 7.22; S 8.16. $C_{20}H_{24}O_5N_2S$. Computed %: N 6.92; S 7.93.

4) N^{ε}-Benzoyl-N^{α}-p-toluenesulfo-d(-)-lysine. 30 g of N^{ε}-benzoyl-d(-)-lysine yielded 35.3 g of a substance with a m.p. of 170°. The m.p. of the product was 171-172° after recrystallization from 60% alcohol. The yield was 75%.

$[\alpha]^{20}_{D}$ +11.4° (0.1054 g substance in 10 ml 0.1 N NaOH; l 1 dm; α +0.12°).
$[\alpha]^{20}_{D}$ + 28.3° (0.4025 g substance in 10 ml 0.5 N NaOH; l 1 dm; α +1.14°).
0.1700 g substance: 8.51 ml 0.1 N HCl. Found %: N 7.00.
$C_{20}H_{24}O_5N_2S$. Computed %: N 6.92.

5) N^{ε}-Benzoyl-N^{α}-(p-acetylaminobenzosulfo)-l(+)-lysine (II,c). 9.4 g of a substance with a m.p. of 190-192° was synthesized by the general condensation procedure from 7.5 g (0.03 mole) of N-benzoyl-l(+)-lysine and 14 g (0.06 mole) of freshly recrystallized p-acetylaminobenzene sulfochloride. Crystallization from 50% alcohol yielded 7.4 g of a substance with a constant m.p. of 194-195°, in the form of flat needles. The yield was 55%.

$[\alpha]^{14}_{D}$ 26.0° (0.1816 g substance in 10 ml 0.1 N NaOH; l 1 dm; α -0.48°).
0.1542 g substance: 10.24 ml 0.1 N HCl. 0.1512 g substance: 0.0780 g $BaSO_4$. Found %: N 9.29; S 7.08. $C_{21}H_{25}O_6N_3S$. Computed %: N 9.40; S 7.18.

6). N^{ε}-Benzoyl-N^{α}-(p-acetylaminobenzosulfo)-d(-)-lysine. 21.4 g of the crude reaction product was synthesized from 15 g of N^{ε}-benzoyl-d(-)-lysine by the same procedure as in the preceding test. Recrystallization from 50% alcohol yielded 19 g (71% of the theoretical) of a substance with the constant m.p. of 196-197°.

$[\alpha]^{20}_{D}$ +26.1° (0.1328 g substance in 10 ml 0.1 N NaOH; l 1 dm; α + 0.35°).
0.1356 g substance: 8.82 ml 0.1 N HCl. Found %: N 9.1.
$C_{21}H_{25}O_6N_3S$. Computed %: N 9.39.

7) N^{ε}-Benzoyl-N^{α}-(p-carbomethoxybenzosulfo)-l(+)-lysine (II, d). 10.4 g of the crude reaction product, with a m.p. of 203° (with decomp.) was synthesized from 10 g (0.04 mole) of N^{ε}-benzoyl-l(+)-lysine and 19.9 g (0.08 mole) of freshly recrystallized p-carbomethoxybenzene sulfochloride. Recrystallization from 96% alcohol yielded 8.5 g of a substance as colorless lamellar crystals, with a m.p. of 210-211°. Evaporation of the crystallization mother liquor in vacuum yielded another 1.4 g of the substance with the same melting point. The total yield of the condensation product was 9.9 g (54%). The substance is insoluble in acetone, chloroform, or ethyl acetate.

$[\alpha]_D^{20}$ −30.7° (0.2114 g substance in 10 ml 0.1 N NaOH; l 1 dm; α −0.65°). 0.1134 g substance: 8.8 ml N_2 (20°, 750 mm). 0.1346 g substance: 0.0688 g $BaSO_4$. Found %: N 8.85; S 7.02. $C_{21}H_{25}O_7N_3S$. Computed %: N 9.07; S 6.92.

8) N^{ε}-Benzoyl-N^{α}-(p-carbomethoxybenzenesulfo)-d(−)-lysine. 5.1 g of a substance with a constant m.p. of 210-211° was secured from 6.7 g of N^{ε}-benzoyl-d(−)-lysine. The yield was 41%.

$[\alpha]_D^{20}$ + 31.2° (0.1860 g substance in 10 ml 0.1 N NaOH; l 1 dm; α +0.58°). 0.1668, 0.1324 g substance: 10.69, 8.51 ml 0.1 N HCl. Found %: N 8.97, 9.00. $C_{21}H_{25}O_7N_3S$. Computed %: N 9.07.

II. Synthesis of N^{α}-Benzosulfo-substituted Derivatives of l and d-Lysine

1) N^{α}-Benzosulfo-l(+)-lysine (III). A solution of 19.4 g of N^{ε}-benzoyl-N^{α}-benzosulfo-l(+)-lysine in 1940 ml of 1 N sodium hydroxide solution was heated for 30 hours over a boiling water bath. After the solution had cooled, it was filtered, and the filtrate was acidulated with concentrated hydrochloric acid until its reaction was acid with Congo red and then evaporated in vacuum at 50-60° to dryness. The residue was triply extracted with a 0.5 N solution of hydrochloric acid, using batches of 150 ml each time. The combined acid extract was cautiously neutralized with concentrated ammonia, while stirred, until its reaction was neutral with bromothymol blue, and then left to stand overnight. The precipitate was filtered out, washed with cold water, and dried. Weight: 11.4 g; m.p. 244° (with decomp.). A single recrystallization from 600 ml of 50% alcohol yielded 9.6 g of a substance with a m.p. of 249-251°. This procedure makes it possible to secure a yield of 68% of N^{α}-benzosulfo-l(+)-lysine, which is 20% higher than the yield of this substance stated in the literature [4].

$[\alpha]_D^{19}$ −44.1° (0.2378 g substance in 10 ml 0.5 N NaOH; l 1 dm; α −1.05°).

2) N^{α}-Benzosulfo-d(−)-lysine. 7.0 g of the crude product, with a m.p. of 240° (with decomp.) was synthesized from 11.5 g of N^{ε}-benzoyl-N^{α}-benzosulfo-d(−)-lysine by the method outlined above. Recrystallization from 50% alcohol yielded 5.1 g (61%) of the theoretical) of a substance with a constant m.p. of 249-250° (with decomp.).

$[\alpha]_D^{20}$ + 43.9° (0.2350 g substance in 10 ml 0.5 N NaOH; l 1 dm; α + 1.03°). 0.2048, 0.1340 g substance: 14.48, 9.42 ml 0.1 N HCl. Found %: N 9.90, 9.84. $C_{12}H_{18}O_4N_2S$. Computed %: N 9.79.

3) N^{α}-(p-Toluenesulfo)-l(+)-lysine (III,b). A solution of 18.6 g of N^{ε}-benzoxy-N^{α}-(p-toluenesulfo)-l(+)-lysine in 1860 ml of 1 N sodium hydroxide solution was heated over a boiling water bath for 30 hours. After the solution had cooled, it was processed as for the synthesis of N^{α}-benzosulfo-l(+)-lysine. This yielded 8.4 g of a substance with a m.p. of 237-245°. A single recrystallization from 50% alcohol yielded 5.2 g (40% of the theoretical) of a substance that crystallized as minute needles, grouped in clusters. M.p. 244° (with decomp.).

$[\alpha]_D^{19}$ −51.6° (0.2363 g substance in 10 ml 0.5 N NaOH; l 1 dm; α −1.22°). 0.1074 g substance: 8.9 ml N_2 (24°, 756 mm). 0.1479 g substance: 0.1138 g $BaSO_4$. Found %: N 9.37; S 10.56. $C_{13}H_{20}O_4N_2S$. Computed %: N 9.33; S 10.69.

4) N^{α}-(p-Toluenesulfo)-d(−)-lysine. 14.2 g of a crude product with a m.p. of 238° (with decomp.) was synthesized from 28.3 g of N^{ε}-benzoyl-N^{α}-(p-toluenesulfo)-d(−)-lysine by the procedure outlined above. Recrystallization from 50% alcohol yielded 9.0 g with a m.p. of 243-244° (with decomp.). The yield was 43%.

$[\alpha]_D^{20}$ +51.6° (0.2014 g substance in 10 ml 0.5 N NaOH; l 1 dm; α + 1.04°). 0.0968 g substance: 6.54 ml 1 N HCl. Found %: N 9.46. $C_{13}H_{20}O_4N_2S$. Computed %: N 9.33.

5) N^{α}-(p-Aminobenzosulfanil)-l(+)-lysine.

a) 6.0 g of N^{ε}-benzoyl-N^{α}-(p-acetylaminobenzosulfo)-l(+)-lysine was dissolved in 400 ml of 1 N sodium hydroxide solution and heated for 15 hours over a boiling water bath. After the solution had cooled, it was processed as specified above for the synthesis of N^{α}-benzosulfo-l(+)-lysine. The precipitated product was filtered out, washed with water, and dried. This yielded 2.2 g of a substance with a m.p. of 240° (with decomp.). The filtrate was evaporated in vacuum to 3/4 of its volume, which yielded another 0.9 g of the same substance (with a decomp. temp. of 238-240°). Recrystallization from water yielded 2.4 g of a substance that crystallized as minute needles with a constant m.p. of 250-251° (with decomp). The yield was 60%.

$[\alpha]_D^{14}$ −15.4° (0.1298 g substance in 10 ml 0.1 N NaOH; l 1 dm; α −0.20°).
$[\alpha]_D^{19}$ − 45.5° (0.1980 g substance in 10 ml 0.5 N NaOH; l 1 dm; α −0.90°). 0.1152 g substance: 14.0 ml N_2 (18°, 752 mm). 0.1240 g substance: 0.0958 g $BaSO_4$. Found %: N 14.0; S 10.60. $C_{12}H_{19}O_4N_3S$. Computed %: N 13.95; S 10.61.

b) A solution of 1.4 g of N^{ε}-benzoyl-N^{α}-(p-carbomethoxybenzosulfo)-l(+)-lysine in 140 ml of 1 N sodium hydroxide solution was heated over a boiling water bath for 15 hours. The usual processing yielded 0.5 g of a substance with a m.p. of 248-252° (with decomp.), which had a m.p. of 251° (with decomp.) after recrystallization from water and exhibited no depression of the melting point when mixed with the N^{α}-(p-aminobenzosulfo)-l(+)-lysine synthesized previously.

6) N^{α}-(p-Aminobenzosulfo)-d(−)-lysine. 14.4 g of N^{ε}benzoyl-N^{α}-(p-acetylaminobenzosulfo)-d(−)-lysine yielded 7.5 g of the crude product. Recrystallization from water yielded 6.5 g (67% of the theoretical) of a substance with a constant m.p. of 251° (with decomp.).

$[\alpha]_D^{20}$ +15.1° (0.1847 g substance in 10 ml 0.1 N NaOH; l 1 dm; α +0.28°).
$[\alpha]_D^{20}$ + 45.9° (0.1964 g substance in 10 ml 0.5 N NaOH; l 1 dm; α + 0.90°). 0.1632, 0.1425 g substance: 16.29, 14.32 ml 0.1 N HCl. Found %: N 13.97, 14.07. $C_{12}H_{19}O_4N_3S$. Computed %: N 13.95.*

SUMMARY

1. Several N^{ε}-benzoyl-N^{α}-benzosulfo-substituted derivatives of l- and d-lysine have been synthesized by condensing N^{ε}-benzoyl-l(+)-lysine and N^{ε}-benzoyl-d(−)-lysine with various sulfochlorides.

2. Saponifying these derivatives with 1 N sodium hydroxide solution yields N^{α}-benzosulfo-substituted derivatives of l- and d-lysine.

3. N^{α}-(p-Aminobenzosulfo)-l(+)-lysine and N^{α}-(p-aminobenzosulfo)-d(−)-lysine

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*The analyses have been performed in our laboratory by P. V. Rasina.

have been synthesized by this method and have been characterized.

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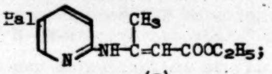
RESEARCHES ON HETEROCYCLIC AMINO DERIVATIVES

VI. DERIVATIVES OF 5-HALOGENO-2-PYRIDONIMIDE

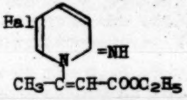
V. F. Kucherov

As was established in our last report [1], condensing acetoacetic ester with 5-halogeno-2-aminopyridines results in a mixture of reaction products, one of which, possessing the empirical formula of $C_{11}H_{13}O_2N_2Hal$, was provisionally assigned the structure of β-(5-halogenopyridinyl-2)-aminocrotonic ester.

This conclusion was based on a fact we had previously observed: that the 5-halogeno-2-aminopyridines exhibited little reactivity in the tautomeric imino form [2]. This fact by itself was far from sufficient to solve the problem of the structure of such compounds conclusively, and the following two formulas are equally probable for them.



(I)

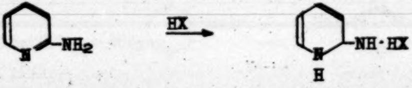


(II)

a) Hal = Cl;
b) Hal = Br;
c) Hal = I.

The present paper deals with the elucidation of the structure of these compounds.

When we consider α-aminopyridine as a cyclic amidine system in which tautomeric conversions are typical, due to the electromeric transformations of the cations of their salts:

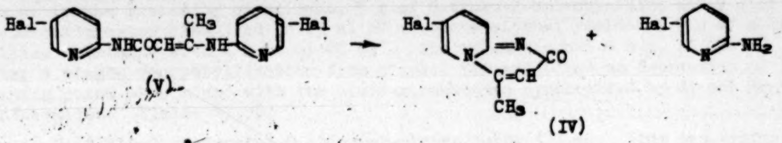


we may assume that it is possible to synthesize compounds of structure (II) by reacting 5-halogeno-2-aminopyridines with acetoacetic ester in the presence of mineral acids.

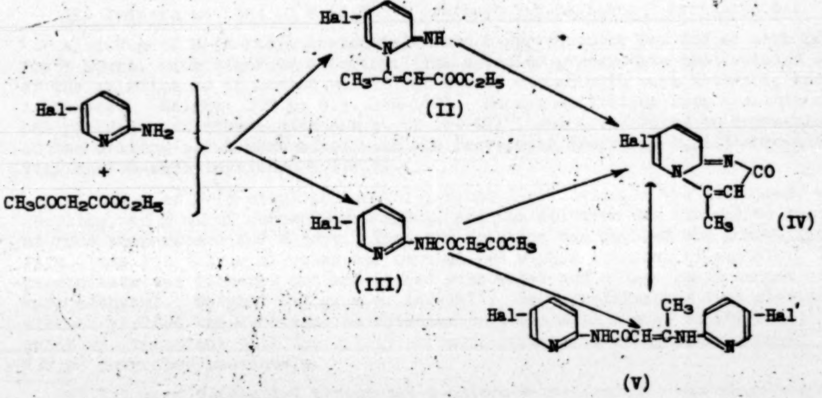
An experimental check established that heating 5-halogeno-2-pyridines with a twofold excess of acetoacetic ester in alcoholic solution containing a small quantity of HCl or H_2SO_4 made it possible to secure up to 50% of a substance with the empirical formula of $C_{11}H_{13}O_2N_2Hal$, which was the same as that synthesized previously by direct thermal condensation. This fact, which tended to support the structure (II), was subsequently corroborated by a study of the transformation reactions of similar compounds.

It was found that all these compounds ($C_{11}H_{13}O_2N_2Hal$) readily split off a molecule of alcohol when treated with concentrated H_2SO_4 in the cold or when heated briefly, being converted into cyclic products (IV) that were the same as those we had synthesized from 5-halogeno-2-acetoacetylaminopyridines (III). The only possible

H_2SO_4 splits off a molecule of 5-halogeno-2-aminopyridine and converts them into 1,2-(3'halogenodivinylene)-6-methylpyrimidones-4 (IV) as follows.



The sum total of the experimental data cited enables us to picture the general scheme of the condensation of 5-halogeno-2-aminopyridines with acetoacetic acid as follows.



This diagram of the transformations conforms to all the experimental data cited above and fully bears out the structure of the resultant condensation products.

EXPERIMENTAL

I. Synthesis of N-(β-Ethyl Crotonate)-5-halogeno-2-pyridonimides

a) N-(β-Ethyl crotonate)-5-iodo-2-pyridonimide (II, c). To a solution of 5.5 g (0.025 mole) of 5-iodo-2-aminopyridine and 8 g (0.06 mole) of acetoacetic ester in 10 ml of absolute alcohol there was added one drop of concentrated H_2SO_4, and the solution was boiled for 6 hours over a water bath and then left to stand overnight. The acicular precipitate was filtered out and washed with a small amount of cold alcohol. Weight: 2.3 g; m.p. 83-85°. The alcohol was driven off in vacuum from the alcoholic mother liquor, the semisolid residue was processed with a small amount of alcohol, and the crystalline residue was filtered out. This yielded another 1.2 g of the substance with a m.p. of 80-85°.

The crystalline product (3.5 g) was recrystallized from a small quantity of alcohol, yielding elongated acicular colorless crystals with a m.p. of 83-84°. Weight: 3.1 g (37.5% of the theoretical).

The substance exhibited no depression of the melting point when mixed with the product with the formula $C_{11}H_{13}O_2N_2I$, previously synthesized by the direct thermal condensation of 5-halogeno-2-aminopyridine with acetoacetic ester.

b) N-(β-Ethyl crotonate)-5-bromo-2-pyridonimide (II,b). By the same procedure as in the preceding experiment, 5 g of 5-bromo-2-aminopyridine and 9 g of acetoacetic ester dissolved in 15 ml of absolute alcohol yielded 3.9 g of a crystalline substance with a m.p. of 85-93°. The substance had a m.p. of 89-90° after a single recrystallization from alcohol and exhibited no depression of the melting point when mixed with the similar substance synthesized by direct thermal condensation. Yield: 41.5%.

c) N-(β-Ethyl crotonate)-5-chloro-2-pyridonimide (II,a). This was synthesized with a yield of 46.5%, from 5-chloro-2-aminopyridine by a procedure resembling that used above. The substance had a m.p. of 84-85° and was identical with the similar substance synthesized by direct thermal condensation.

II. Transformations of N-(β-Ethyl crotonate)-5-halogeno-2-pyridonimides

a) 1.0 g of N-(β-Ethyl crotonate)-bromo-2-pyridonimide was boiled with 20 ml for 4 hours, with vigorous stirring. The acicular precipitate that settled out of the solution as it cooled was filtered out, washed with warm methanol, and desiccated. Weight: 0.5 g; m.p. 140-148°. Recrystallization from absolute alcohol yielded a substance with a m.p. of 169-171°, which exhibited no depression of the melting point when mixed with the previously described 1,2-(3'-bromodivinylene)-6-methylpyridone-4 (IV,b).

b) 1.0 g of N-(β-ethyl crotonate)-5-bromo-2-pyridonimide was dissolved, with chilling, in 3 ml of concentrated H_2SO_4, and the solution was allowed to stand at room temperature for 2 days. Then the solution was chilled and poured into five times its volume of water and neutralized with a solution of ammonia. The precipitate was filtered out and washed with water and with a small amount of warm methanol. Weight: 0.7 g; m.p. 142-147°. Recrystallization from absolute alcohol yielded the substance as acicular crystals with a m.p. of 169-170°, which was identical with the 1,2-(3'-bromodivinylene)-6-methylpyrimidone-4 (IV,b) described previously.

c) 1.1 g of N-(β-ethyl crotonate)-5-chloro-2-pyridonimide was dissolved in 4 ml of concentrated H_2SO_4, and the solution was heated for 15 minutes over a boiling water bath. The processing outlined above and recrystallization of the resultant precipitate from absolute alcohol yielded 0.5 g of a substance with a m.p. of 166-167°, which exhibited no depression of the melting point when mixed with the 1,2-(3'-chlorodivinylene)-6-methylpyrimidone-4 described earlier.

d) 1.0 g of N-(β-ethyl crotonate)-5-bromo-2-pyridonimide was boiled with 5 ml of a 50% potassium hydroxide solution. Dissolution was gradual and was accompanied by considerable darkening of the solution and the evolution of ammonia. The products of this reaction were not investigated further.

III. Synthesis of 5'-Halogenopyridylamides of β-(5-Halogenopyridyl-2)-aminocrotonic Acids and Their Transformations

a) A mixture of 1.0 g of 5-bromo-2-acetoacetylaminopyridine and 0.7 g of 5-bromo-2-aminopyridine was dissolved in 10 ml of warm absolute alcohol, 1 ml of concentrated H_2SO_4 was added, and the solution was boiled over a water bath.

As the reaction progressed, a white amorphous precipitate gradually settled out of the solution. After boiling had gone on for 3 hours, the precipitate was filtered out and washed with warm alcohol. Weight: 1.1 g; m.p. 216-220°. Recrystallization from chloroform yielded 0.9 g of a substance (55.5% of the theoretical) with a m.p. of 240-241°, which was identical with the 5'-bromopyridylamide of β-(5-bromopyridyl-2)-aminocrotonic acid (V) described previously.

b) One drop of concentrated H_2SO_4 was added to a solution of 1.0 g of 5-bromo-2-acetoacetylaminopyridine and 0.5 g of 5-chloro-2-aminopyridine in 20 ml of absolute alcohol, and the whole was boiled for 3 hours. The resultant precipitate was filtered out and washed with hot alcohol. Weight: 1.0 g; m.p. 230-233°. Recrystallization from chloroform yielded 0.8 g (56% of the theoretical) of a substance with a m.p. of 243-244°, the analysis of which proved its identity with the 5'-bromopyridylamide of β-(5-chloropyridyl-2)-aminocrotonic acid (V,a).

0.1262 g substance: 17.15 ml N_2 (22.5°, 758 mm). Found %: N 15.49.
$C_{14}H_{12}ON_4ClBr$. Computed %: N 15.24.

c) By a similar procedure 5-chloro-2-acetoacetylaminopyridine and 5-bromo-2-aminopyridine combined to form 52% of a substance with a m.p. of 241-242°, the analysis of which proved its identity with the 5'-chloropyridylamide of β-(5-bromopyridyl-2)-crotonic acid (V,b).

0.1252 g substance: 16.9 ml N_2 (22.5°, 760 mm). Found %: N 15.43.
$C_{14}H_{12}ON_4ClBr$. Computed %: N 15.24.

d) A solution of 1.0 g of 5-chloro-2-acetoacetylaminopyridine and 0.6 g of 5-chloro-2-aminopyridine in 20 ml of absolute alcohol was boiled with 2 drops of concentrated H_2SO_4 for 12 hours. The precipitate had a m.p. of 241-242° after recrystallization from chloroform and was identical with the 5'-chloropyridylamide of β-(5-chloropyridyl-2)-aminocrotonic acid described previously. The yield was 46% of the theoretical.

e) By a similar procedure an individual substance with a m.p. of 231-232°, the analysis of which established its identity with the 5'-chloropyridylamide of β-(5-iodopyridyl-2)-aminocrotonic acid (V,c), was synthesized, with a yield of 42.5% of the theoretical, from 5-chloro-2-acetoacetylaminopyridine and 5-iodo-2-aminopyridine.

0.1218 g substance: 14.7 ml N_2 (17.5°, 746 mm). Found %: N 13.81.
$C_{14}H_{12}ON_4ClI$. Computed %: N 13.51.

f) A solution of 1.5 g of the 5'-chloropyridylamide of β-(5-chlorppyridyl-2)-aminocrotonic acid in 6 ml of concentrated H_2SO_4 was heated for 15 minutes over a boiling water bath. The solution was then poured into a fivefold volume of cold water and neutralized with ammonia, and the resultant precipitate was filtered out and washed with cold alcohol. Weight: 0.7 g; m.p. 148-152°. The substance had a m.p. of 167-169° after recrystallization from alcohol and exhibited no depression of the melting point when mixed with 1,2-(3'-chlorodivinylene)-6-methylpyrimidone-4 (IV, a) described previously.

SUMMARY

1. The structure of $C_{11}H_{13}O_2N_2Hal$, the low-fusing condensation product of 5-halogeno-2-aminopyridines with acetoacetic ester has been established as that of a N-(β-ethyl crotonate)-5-halogeno-2-pyridonimide.

2. A general method is set forth for synthesizing N-(β-ethyl crotonate)-5-halogeno-2-pyridonimides (II) and the 5'-halogenopyridylamides of β-(5-halogenopyridyl)-aminocrotonic acid (V).

3. The general diagram for the transformations of the reaction products of the thermal condensation of the 5-halogeno-2-aminopyridines with acetoacetic ester is furnished.

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*See CB translation p. 1957 ff.

THE AZO DYES OF 2,8-AMINONAPHTHOL AND OF SOME OF ITS DERIVATIVES

II. INTERACTION OF THE SULFO ACIDS OF 2,8-AMINONAPHTHOL WITH DIAZO COMPOUNDS

V. V. Perekalin and L. N. Kononova

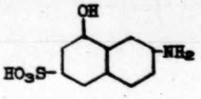
In the preceding communication one of the present authors demonstrated that when 2,8-aminonaphthol reacts with diazobenzene, it forms two monoazo dyes: ortho amino and para hydroxy isomers. Coupling the para hydroxyazo dye with another mol of diazobenzene yielded an ortho, para, hydroxy disazo dye; no ortho amino azo dye was formed, however.

As we know, one of the sulfo acids of 2,8-aminonaphthol – 2,8-aminonaphthol-6-sulfo acid (gamma acid) – or more accurately, the monoazo dyes synthesized from this compound and widely employed as azo constituents in the synthesis of mono and polyazo sulfo acid dyes, does not enter into azo coupling and does not form a disazo dye [2] when reacted with another mol of a diazo compound, though there are no visible obstacles to this reaction. This unusual behavior of gamma acid has not been explained in the literature, although commented on by several authors [3,4].

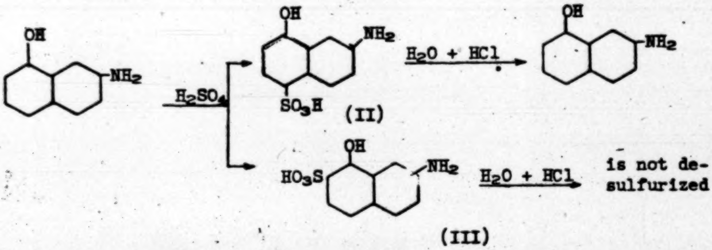
We have advanced a hypothesis to explain the nature of the reaction with diazo compounds of the sulfo acids of various aminonaphthols: in particular, we have explained the reason why gamma acid cannot form disazo dyes [5]. Hence, an investigation of the reaction of the sulfo acids of 2,8-aminonaphthol with diazo compounds, with the objective of providing an experimental check of this hypothesis was a logical extension of our research on the azo coupling of 2,8-aminonaphthol.

We had at our disposal three sulfo acids of 2,8-aminonaphthol described in the literature: gamma acid (I), on which sufficient research has been done; 2,8-aminonaphthol-5-sulfo acid (II); and 2,8-aminonaphthol-7-sulfo acid (III). Practically no work has been done on the latter two sulfo acids, all we know being that they are both secured simultaneously when 2,8-aminonaphthol is sulfonated with concentrated sulfuric acid, and that one of them is freely soluble in water, while the other is only very slightly soluble. But which one was the 5-sulfo acid and which the 7-acid has remained unknown. By analogy with the properties of the sulfo acids of 1-naphthol (1,4-naphtholsulfo acid is freely soluble in water [7,8], while 1,2-naphtholsulfo acid's solubility is much worse [9]), it might have been assumed that the sulfo acid that is freely soluble in water is the p-hydroxysulfo acid, i.e., 2,8-aminonaphthol-5-sulfo acid, and that the acid that is slightly soluble in water is the o-hydroxysulfo acid, i.e., 2,8-aminonaphthol-7-sulfo acid. This analogy was not enough, however, for conclusive findings re the structure of these sulfo acids.

The ease with which the sulfo groups at the α-position in various naphthalene derivatives can be desulfurized is a matter of common knowledge [10]; the sulfo group in the β-position cannot be hydrolyzed under the same conditions, and, in general, is hard to eliminate [11,12]. Desulfurizing the sulfo acid II, which is freely soluble in water, yielded 2,8-aminonaphthol, whereas the sulfo acid III, which is slightly soluble, was recovered unchanged in an analogous test and did not yield a trace of 2,8-aminonaphthol. Hence, the sulfo acid II was 2,8-aminonaphthol-5-sulfo acid, and the sulfo acid III was 2,8-aminonaphthol-7-sulfo acid.



(I)



The potentiometric titration curves of these sulfo acids (Fig. 1) revealed a very specific difference in their properties and, hence, in their structure: the titration curve of the sulfo acid (II) exhibited two potential jumps, the sulfo acid remaining in solution; titration of the sulfo acid (III) involved three potential jumps, and at the end of titration the sulfo acid was thrown down as a precipitate while the pH rose slightly. The equivalence points of the titration curves of these sulfo acids are located at different pH values.

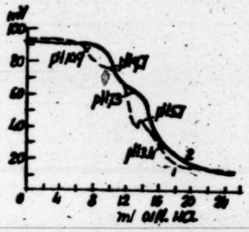


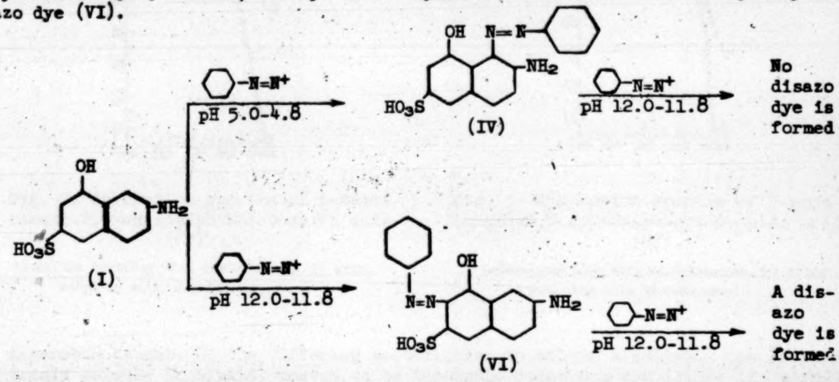
Fig. 1. Potentiometric titration curves.

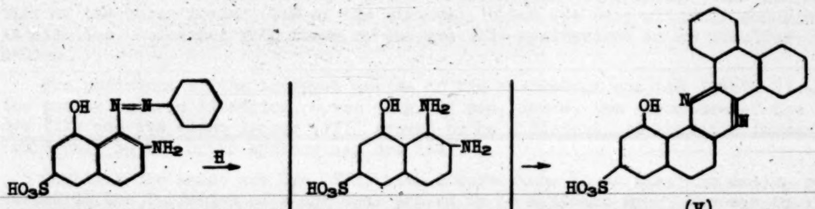
1) 2,8-aminonaphthol-5-sulfo acid;
2) 2,8-aminonaphthol-7-sulfo acid.

We then investigated the reaction of these sulfo acids with diazobenzene. We began by checking the extremely scanty data in the literature on the inability of gamma acid to enter into disazo coupling [3,4]. Coupling gamma acid at pH 5.0–4.8 yielded two monoazo dyes, which were separable owing to their differing solubilities in dilute alkalies; one, readily soluble in alkalies, proved to be an ortho amino azo dye (IV), since it yielded a phenanthrazine derivative (V) after it had been reduced to a diaminonaphtholsulfo acid and the latter had been condensed with a bisulfite derivative of phenanthraquinone. The properties of the other dye (7% of the mixture) coincided with those of the dye (VI) secured at a pH of 12.0–11.8.

It should be noted that the usual method of establishing the purity of a substance – determining its melting point – could not be used here, since neither the similar sulfo acids nor the azo dyes possessed sharp melting points, owing to the presence of the sulfo group. We therefore had to resort to other ways of establishing the individual nature of the synthesized dyes. determining the position of the longwave maxima in their absorption spectra at various refining stages, and potentiometric titration.

Coupling gamma acid in an alkaline medium of pH 12.0-11.8 resulted in the synthesis of a homogeneous monoazo dye, whose properties differed from those of the ortho amino isomers (V). The azo group in this dye might be in either the ortho or the para positions to the hydroxyl group; we know, however, that when 1,3-naphthosulfo acid is coupled with diazobenzene, only an ortho hydroxy azo dye results [13]. Hence, the dye we had synthesized was also an ortho hydroxy azo dye (VI).





Both of the monoazo dyes were reacted with another mol of diazobenzene in an alkaline medium and in pyridine; as stated in the literature, the results were negative: the monoazo dyes derived from gamma acid did not enter into azo coupling with diazobenzene and did not yield disazo dyes. The quantity of dyes present hardly changed before and after coupling, nor did the positions of the longwave maxima vary in their absorption spectra. (Figs. 2 and 3).

Coupling the other two sulfo acids with diazobenzene yielded different results. Owing to the high solubility of 2,8-aminonaphthol-5-sulfo acid (II) and, hence, of the dye in water, the sulfo acid II was coupled with diazobenzene in more highly concentrated solutions (0.5 N) than usual. Coupling the sulfo acid II at a pH of 5.0-4.8 resulted in the synthesis of two azo dyes, which were

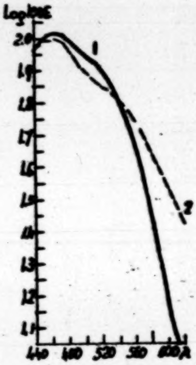


Fig. 2. Absorption spectra of 1-benzeneazo-2,8-aminonaphthol-6-sulfo acid (IV)

1) Before reacting with diazobenzene; 2) after reacting with diazobenzene

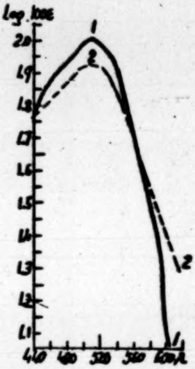


Fig. 3. Absorption spectra of 7-benzeneazo-2,8-aminonaphthol-6-sulfo acid (VI).

1) Before reacting with diazobenzene; 2) after reacting with diazobenzene

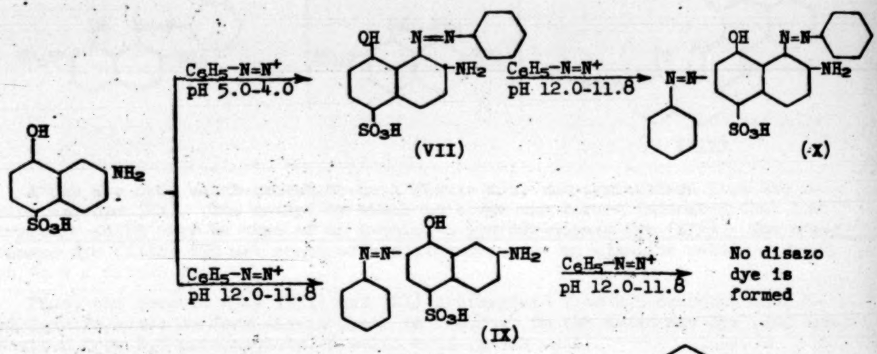
separable because of the differing solubilities in dilute alkalies. One of them, freely soluble in alkali, proved to be the ortho amino azo dye (VII); its structure was established by reducing it to diaminonaphthol and condensing the latter with phenanthraquinone, yielding a phenanthrazine derivative (III). The properties of the other isomer (11% of the mixture), which was only slightly soluble in alkalies, coincided with those of the dye (IX) synthesized in an alkaline medium.

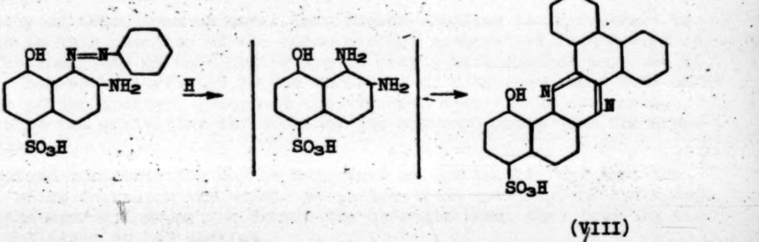
The positions of the longwave maxima of the absorption spectra (Table 2) and the potentiometric titration curves (Fig. 4) and, hence, the structure of the dye (IX) and its amino isomer (VII) proved to be different, so that the former could only be the ortho hydroxy azo dye (IX).

Coupling the amino azo dye (VII) with diazobenzene in an alkaline medium resulted in the formation of a dye that proved to be a disazo dye. The way in which this disazo dye was formed meant that it could only possess the structure of an o-amino o-hydroxy disazodye (X).

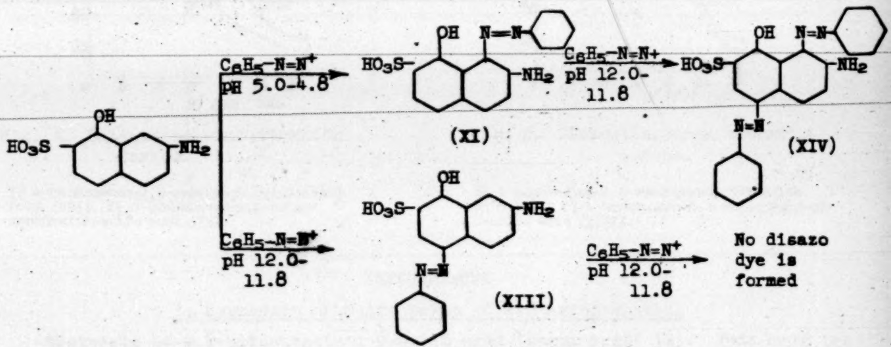
The reaction of the ortho hydroxy isomer (IX) with diazobenzene in an alkaline medium resulted in the recovery of the initial azo dye from the reaction mixture. In this case disazo coupling might take place as the result of the displacement of the sulfo group located at the α-position. Similar cases are known: coupling 2,1-naphtholsulfo acid with diazobenzene, for example, results in the formation of 1-benzeneazo-2-naphthol [14]; in our experiment, however, no displacement occurred.

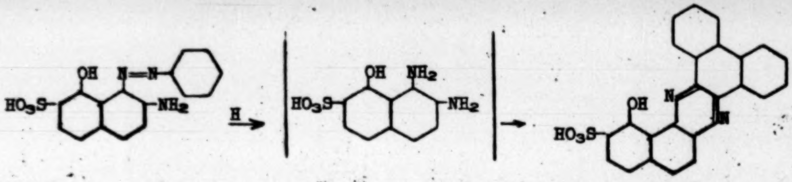
When the third sulfo acid – 2,8-aminonaphthol-7-sulfo acid (III) – was coupled with diazobenzene, it behaved like the preceding isomer. At a pH of 5.0-4.8 we secured a dye that separated into two isomers: one, an ortho amino azo dye (XI), yielded a phenanthrazine derivative (XII) after having been reduced and


$C_6H_5-N=N^+$
pH 5.0-4.0
(VII)
$C_6H_5-N=N^+$
pH 12.0-11.8
(X)
$C_6H_5-N=N^+$
pH 12.0-11.8
(IX)
$C_6H_5-N=N^+$
pH 12.0-11.8
No disazo dye is formed



condensed with phenanthraquinone. The isomer that was less soluble in alkalies (13% of the mixture) proved to be identical with the dye (XIII), synthesized from this sulfo acid in an alkaline medium. The positions of the longwave maxima in the absorption spectra of this dye (Table 2) and its potentiometric titration curve, and hence, its structure, all indicate that this dye is not the same as its amino isomer (XI), but can only be a p-hydroxyazo dye (XIII).


$C_6H_5-N=N^+$
pH 5.0-4.8
(XI)
$C_6H_5-N=N+$
pH 12.0-11.8
(XIV)
$C_6H_5-N=N^+$
pH 12.0-11.8
(XIII)
$C_6H_5-N=N^+$
pH 12.0-11.8
No disazo dye is formed



(XII)

A new azo dye, which proved to be a disazo dye, was synthesized from the o-amino azo dye (XI). The method by which this dye was formed indicated that its structure could only be that of an o-amino-p-hydroxy-disazo dye (XIV). The other monoazo dye (XIII) did not react with diazobenzene in an alkaline medium and did not form a disazo dye.

Thus, the monoazo dyes (VII) and (XI) synthesized from 2,8-aminonaphthol-5- and 7-sulfo acids do form disazo dyes, in contrast to the amino azo dye (IV) synthesized from 2,8-aminonaphthol-6-sulfo acid (gamma acid).

The ability of these dyes to enter into disazo coupling is in contrast to the inertness in this reaction of the amino azo dye synthesized from 2,8-aminonaphthol. The inability of this latter dye to couple with another molecule of diazobenzene has been attributed to the formation of a hydrogen bond between the hydrogen atom of the hydroxyl group and the nitrogen atom of the azo group, which diminishes the activating influence of the hydroxyl group upon the aromatic ring [1].

This apparent contradiction may be explained as due to the fact that the sulfo group, which increases the acidic properties (the mobility) of the hydrogen atom in the hydroxyl group and breaks the hydrogen bond, thus lowering the stabilizing influence it had exerted.

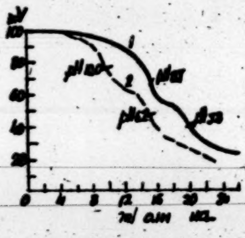


Fig. 4. Potentiometric titration curves.

1) 1-benzeneazo-2,8-aminonaphthol-5-sulfo acid (VII); 2) 7-benzeneazo-2,8-aminonaphthol-5-sulfo acid (IX).

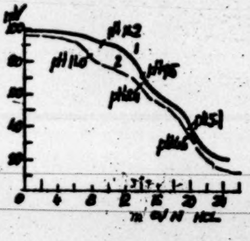


Fig. 5. Potentiometric titration curves.

1) 1-Benzeneazo-2,8-aminonaphthol-7-sulfo acid (XI); 2) 5-benzeneazo-2,8-aminonaphthol-7-sulfo acid (XIII).

EXPERIMENTAL

I. Synthesis of Sulfo Acids of 2,8-Aminonaphthol

Synthesis of 2,8-aminonaphthol-6-sulfo acid (gamma acid) (I). This acid was synthesized by alkaline fusion of the sodium salt of 2-naphthylamine-6,8-disulfo acid [15,16]. The gamma acid consisted of minute light-gray crystals after it had been purified by repeated crystallization from water.

Synthesis of 2,8-aminonaphthol was effected by the alkaline fusion of the sodium salt of 2-naphthylamine-8-sulfo acid [1]

Synthesis of 2,8-aminonaphthol-5- and 7-sulfo acids (II and III), was effected by sulfonating 2,8-aminonaphthol at 0-3° and 20-30°, respectively.

a) 7.95 g of 2,8-aminonaphthol (0.05 mole) was gradually poured into 16 ml of 96% sulfuric acid (5 moles excess) at 0-3°, with stirring; then the reaction mixture was stirred for 4 hours. After testing for completeness of sulfonation (solubility in a 10% soda solution of the precipitate thrown down when a drop of the sulfo mass is put in 2 ml of water), the sulfo mass was poured into 100 ml of water (four times its volume), the precipitate thrown down being filtered out and washed with water. The yield of the sulfo acid (III) that is sparingly soluble in water (assumed to be 2,8-aminonaphthol-7-sulfo acid) was 7.7 g (65% of the theoretical). The sodium salt of the other sulfo acid (II), freely soluble in water (assumed to be 2,8-aminonaphthol-5-sulfo acid) was recovered from the filtrate by salting out. The yield was 2.9 g (16% of the theoretical).

b) Sulfonation of 2,8-aminonaphthol at 20-30°. This was done like the sulfonation described under a). The yield of the sulfo acid sparingly soluble in water was 5.98 g (50% of the theoretical), and that of the acid freely soluble in water was 4.47 g (35% of the theoretical). The sparingly soluble sulfo acid was reprecipitated from a 10% soda solution by 10% hydrochloric acid and then recrystallized from water (2.39 g from 100 ml of water); the sodium salt of the freely soluble sulfo acid was likewise recrystallized from water (2.6 g from 40 ml of water).

The structure of the 5- and 7-sulfo acid of 2,8-aminonaphthol was established by desulfurizing them.

a) 2.63 g (0.01 mole) of the sodium salt of the hypothetical 2,8-aminonaphthol-5-sulfo acid (II) was mixed with 20 ml of 20% hydrochloric acid; the suspension was heated with a reflux condenser for 28 hours over a boiling water bath; after it had cooled it was filtered. The residue on the filter was 0.4 g. Neutralization of the filtrate with a 10% solution of sodium acetate yielded minute light crystals, the m.p. of which was 156° after recrystallization from water, which exhibited no depression when mixed with 2,8-aminonaphthol (m.p. 156°).

b) 8 ml of 10% sodium hydroxide and then 20 ml of 20% hydrochloric acid were added to 2.39 g (0.01 mole) of the hypothetical 2,8-aminonaphthol-7-sulfo acid (III); the suspension was heated for 28 hours over a boiling water bath; it was filtered after it had cooled. The residue of 2.2 g on the filter was readily soluble in a 10% soda solution and was precipitated from the solution by concentrated hydrochloric acid. No 2,8-aminonaphthol was recovered when the filtrate was neutralized with sodium acetate.

II. Experimental Procedure in the Synthesis of Azo Dyes and the Determination of Their Properties

The 2,8-aminonaphthol-6- and 7-sulfo acids were used as the free sulfo acids, while the 2,8-aminonaphthol-5-sulfo acid was used in the form of its sodium salt. In coupling we took 0.01 mole of each of the aminonaphtholsulfo acids (2.39 g, based on the chemically pure products), using them in the form of 0.1 N solutions; in the coupling of the dyes we also took 0.01 mole (3.43 g), using that quantity to prepare 0.1 N solutions.

Coupling was done at fixed pH values; the coupling media were prepared from these weighed quantities as follows.

1) pH 2.5-2.3 [*] (hydrochloric acid medium). The weighed sample was dissolved in 8 ml of 10% sodium hydroxide and acidulated with 8.6 ml of 10% hydrochloric acid (2 moles excess), after which the suspension was diluted to 100 ml with water.

2) pH 5.0-4.8 (sodium acetate and acetic-acid medium). The weighed sample was mixed with 54.4 ml of a 10% solution of sodium acetate (3 moles excess) and 6 ml of 10% acetic acid (total excess: 2 moles). The suspension was diluted to 100 ml with water and heated to 50-60°; the solution was filtered after it had cooled. In coupling the sodium salt of 2,8-aminonaphthol-5-sulfo acid we took 40.8 ml of 10% sodium acetate and 12 ml of 10% acetic acid.

3) pH 5.4-5.2 (sodium-acetate medium). The weighed sample was mixed with 54 ml of a 10% solution of sodium acetate (3 moles excess) and dissolved in 100 ml of water.

4) pH 12.0-11.8 (alkaline medium). The weighed sample was dissolved in 16 ml of a 10% solution of sodium hydroxide (2 moles excess) and diluted to 100 ml with water. In coupling the sodium salt of 2,8-aminonaphthol-5-sulfo acid we took 12 ml of a 10% solution of sodium hydroxide (2 moles excess); the monoazo dye was dissolved in 24 ml of a 10% solution of sodium hydroxide (4 moles excess) for disazo coupling.

5) Pyridine medium, pH 10.25-7.4. The weighed sample was dissolved in 200 ml of pyridine.

The diazo constituent used was diazobenzene, which formed the simplest dyes, most convenient for subsequent investigation. A 0.1 N solution of diazobenzene was prepared by diazotizing aniline in the customary manner. The solutions of the azo constituents were combined with 100 ml of the 0.1 N solution of diazobenzene (equimolar quantities) containing a slight excess of hydrochloric acid (pH 1.5).

The time during which the diazo solution was added and the duration of the ensuing coupling were governed in each case by the course of the coupling reaction, which was carried out at 5-10° with constant stirring. The first drop of the diazobenzene colored the reaction mixture red or reddish-purple. The resulting dyes precipitated out or remained in solution, depending upon the pH of the medium and the solubility of the dye.

When coupling was complete, the mixture was filtered; the dyes were recovered from the filtrates by acidulating the latter with 10% hydrochloric acid. The residues left on the filter were dissolved in an excess of 1% sodium hydroxide solution and precipitated with concentrated sulfuric acid at 50-60°; after the excess acid had been washed out, the precipitates were recrystallized from ethyl alcohol and dried at 120° to constant weight. Any departures from this procedure are specially mentioned below.

The absorption spectra of the dyes were determined in a Koenig-Martens spectrophotometer.

The State Institute of Applied Chemistry type of lamp potentiometer was used in the potentiometric titration of the sulfo acids and dyes, as well as in determining the pH of the medium. A weighed sample of the substance was dissolved in a 0.1 N sodium hydroxide solution and titrated with a 0.1 N solution of hydrochloric acid. The equivalence points on the titration curves were determined

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[*] The first figure is the pH before coupling, the second, the pH after coupling.

TABLE 1

Medium pH in the Syntheses of Azo Dyes and Their Yields

No.	Dye	pH	Yield, % of theoretical
1	1-Benzeneazo-2,8-aminonaphthol-6-sulfo acid (IV) ...	5.4-5.2	85
2	7-Benzeneazo-2,8-aminonaphthol-6-sulfo acid (VI) ...	12.1-11.8	81
3	1-Benzeneazo-2,8-aminonaphthol-5-sulfo acid (VII) ..	5.0-4.8	62
4	7-Benzeneazo-2,8-aminonaphthol-5-sulfo acid (IX) ...	12.0-11.8	87
5	1,7-Disbenzeneazo-2,8-aminonaphthol-5-sulfo acid (X)	12.0-11.8	45
6	1-Benzeneazo-2,8-aminonaphthol-7-sulfo acid (XI) ...	5.0-4.8	45
7	5-Benzeneazo-2,8-aminonaphthol-7-sulfo acid (XIII) .	12.0-11.8	80
8	1,5-Disbenzeneazo-2,8-aminonaphthol-7-sulfo acid (XIV)	12.0-11.8	71

TABLE 2

Positions of Longwave Maxima and Colors of Solutions

Dye	λ mμ	10% NaOH	36% H_2SO_4	37% HCl	100% CH_3COOH
IV	500	Brownish-red	Reddish-purple	Reddish-purple	Slightly soluble, brown
VI	510	Orange-red	Intense orange-red	Sparingly soluble, yellow	Slightly soluble, orange
VII	490	Red	Brownish-red	Red	Intense red
IX	500	Crimson	Brownish-red	Red	Red
X		Sparingly soluble, reddish-purple	Intense crimson	Slightly soluble, red	Crimson
XI	490	Red	Brownish-purple	Brownish-red	Crimson
XIII	500	Red	Reddish-brown	Pink	Red
XIV		Red	Purple	Reddish-brown	Brownish-purple

graphically by the method of normals, by means of differential curves, and by the method of derivatives. All three methods yielded results that were in agreement within the limits of experimental error (the second method exhibiting some discrepancies on occasion). The titration data were used to calculate the molecular weights of the compounds under test.

III. Synthesis of Azo Dyes

1. Synthesis of 1-Benzeneazo-2,8-aminonaphthol-6-sulfo acid (IV)

Coupling 2,8-Aminonaphthol-6-sulfo acid (gamma acid) (I) at a pH 2.5-2.3. The diazobenzene was added in the course of 30 minutes, after which the mixture was stirred for 2.5 hours. Filtration and reprecipitation from an alkaline solution with hydrochloric acid yielded 0.31 g (9% of the theoretical) of the dye.

Coupling of gamma acid at pH 5.0-4.8. The dye precipitated gradually as the diazobenzene was added (during the course of 30 minutes); after two hours of stirring, the precipitated sodium salt of the dye, which was readily soluble in water, was filtered out. The filtrate yielded a negligible additional quantity of the dye, its overall yield being 3.0 g. The sodium salt of the dye was dissolved in 200 ml of water at 30-40° and filtered; the filtrate was processed with concentrated hydrochloric acid at 50-60°, which yielded 2.9 g (85% of the theoretical) of the dye (the supposed dye IV). The dye, a dark, bronzy powder, was moderately soluble in ethyl alcohol and acetone and was insoluble in benzene or chlorobenzene.

The position of its longwave maximum and the colors of its solutions, as well as of all the other dyes described below, are listed in Table 2.

The residue on the filter (0.24 g – 7% of the mixture) was processed twice with 50 ml of 1% sodium hydroxide solution, the dye dissolving completely, and then it was reprecipitated with concentrated hydrochloric acid; the position of the longwave maximum and the colors of solutions of this dye were the same as those of the dye (VI) synthesized in an alkaline medium.

Establishing the structure of the dye IV – Synthesis of 8-hydroxy-1,2-naphthophenanthrazine-7-sulfo acid (V).

a) Reducing the dye. 0.34 g of the dye (0.001 mole) was dissolved in 20 ml of water and 2 ml of a 25% solution of ammonia. Zinc dust was gradually added to the brown solution, after which the faintly colored solution was filtered and cautiously acidulated with 10% acetic acid, causing the partial precipitation of the diaminonaphtholsulfo acid.

b) Condensation with phenanthraquinone. The suspension of the diaminonaphtholsulfo acid, with a slightly acetic-acid reaction, was heated to boiling (nearly all the sulfo acid dissolved) and quickly mixed at 70-80° with 20 ml of a bisulfite solution of 0.2 g of phenanthraquinone. The yellow-brown leaflets of the phenanthrazine, which dissolved in concentrated sulfuric acid, turning it purple, slowly settled out. The yield was 0.15 g (35% of the theoretical).

Attempt to synthesize a disazo dye from the dye IV.

a) At a pH of 12.0-11.8. After the diazobenzene had been added in the course of 30 minutes, the mixture was stirred for 12 hours and then filtered; no precipitate was found on the filter, 3.1 g of a dye (90% of the initial amount) being recovered. The positions of the longwave maxima of the absorption spectra and the colors of the solutions of this dye were the same as those of the original.

b) In a pyridine medium (pH 10.25-7.4). Coupling was continued for 12 hours, after which the reaction mixture was filtered (no precipitate being found) and diluted with 600 ml of water; acidulation with concentrated hydrochloric acid until the reaction with Congo red was slightly acid yielded 3.02 g of a dye (88% of the initial amount). The positions of the longwave maxima of the absorption spectra and the colors of the solutions of this dye were the same as those of the original.

2. Synthesis of 7-benzeneazo-2,8-aminonaphthol-6-sulfo acid (VI).

Coupling gamma acid at pH 12.0-11.8. The diazobenzene was added during 15 minutes; a red-orange dye settled out of the solution after 2 hours of coupling.* The yield was 2.8 g (81% of the theoretical).

Attempt to synthesize a disazo dye from the dye VI at pH 12.0-11.8. The dye was dissolved in 24 ml of a 10% sodium hydroxide solution (4 moles excess), diluted with water to 500 ml, and coupled with diazobenzene for 12 hours; then the solution was filtered (no precipitate being found on the filter). This yielded 2.9 g of a dye (84% of the initial amount), the positions of the longwave maxima of the absorption spectra and the colors of the solutions of this dye were the same as those of the original.

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*Whenever no mention is made of the method of recovering and purifying the dye, these operations were performed as described in the section entitled "Experimental Procedure in the Synthesis of Azo Dyes and the Determination of their Properties."

3. Synthesis of 1-benzeneazo-2,8-aminonaphthol-5-sulfo acid (VII)

Coupling the sodium salt of 2,8-aminonaphthol-5-sulfo acid (II) at a pH of 5.0-4.8. The solution of the diazo compound was added to the 0.5 N solution of the sulfo acid for 3 hours, and then the mixture was stirred for 12 hours and filtered. The precipitate yielded 1.9 g of the sodium salt of the dye, the filtrate yielding 0.5 g, for a total yield of 2.4 g.

The mixture was separated into two individual dyes: a readily alkali-soluble dye (2.1 g, 62% of the theoretical), which was assumed to be the dye VII, and a sparingly alkali-soluble dye (0.24 g, 11% of the mixture). The properties of this latter dye were found to be the same as those of the dye IX synthesized in an alkaline medium.

Establishing the structure of the dye VII - synthesis of 8-hydroxy-1,2-naphthophenanthrazine-7-sulfo acid (VIII).

a) Reducing the dye. 0.34 g of the dye, dssolved in 10 ml of water at 50-60°, was reduced with 0.75 g of stannous chloride, previously dissolved in 5 ml of 37% hydrochloric acid; the brown solution was decolorized almost instantaneously. As the solution cooled, an amorphous precipitate of a diaminonaphtholsulfo acid settled out; it was filtered out and dissolved in 10 ml of hot water.

b) Condensation with phenanthraquinone. 10 ml of the diaminonaphtholsulfo acid was mixed at 80-90° with 2 g of phenanthraquinone, dissolved in 60 ml of bisulfite solution. Heating for a few minutes at this temperature resulted in the precipitation of olive-green crystals of the phenanthrazine, which dissolved in concentrated sulfuric acid, turning the solution blue. The yield was 0.12 g (28% of the theoretical).

Coupling the dye VII at a pH of 12.0-11.8 - synthesis of 1,7-disbenzeneazo-2,8-aminonaphthol-5-sulfo acid (X).

The diazobenzene solution was added to the solution of the dye in the course of 3 hours; 12 hours later a dye that was sparingly soluble in alkalies precipitated out. The yield was 2 g (45% of the theoretical).

4. Synthesis of 7-benzeneazo-2,8-aminonaphthol-5-sulfo acid (IX).

Coupling the sodium salt of the sulfo acid II at a pH of 12.0-11.8. A 0.75 N solution of the sulfo acid was coupled with diazobenzene for 3 hours; after 12 hours of stirring the mixture was filtered (no precipitate was found on the filter), and 3 g of a dye (87% of the theoretical) was recovered from it.

Attempt to synthesize a disazo dye from the dye IX at a pH of 12.0-11.8.

The alkaline solution was filtered after 3 hours of coupling (no precipitate was found on the filter); acidulating the filtrate with hydrochloric acid yielded 3.5 g of a dye (93.3% of the initial quantity). The positions of this dye's longwave maxima and its solution colors were the same as those of the original.

5. Synthesis of 1-benzeneazo-2,8-aminonaphthol-7-sulfo acid (XI).

Coupling 2,8-aminonaphthol-7-sulfo acid (III) at a pH of 5.0-4.8. The 2.33 g of dye that was precipitated after 12 hours of coupling was filtered out. This dye was a mixture, which was then separated into a dye that was freely soluble in dilute alkalies - the hypothetical dye XI (1.5 g, 45% of the theoretical) - and an isomer that was sparingly soluble in dilute alkalies (13% of the mixture). The properties of this latter day and those of the dye XIII synthesized in an alkaline medium were identical.

Establishing the structure of the dye XI – synthesis of 8-hydroxy-1,2-naphthophenanthrazine-7-sulfo acid (XII).

The dye was reduced, and the diaminonaphthol was condensed with phenanthraquinone as described for the dye VII. The yield of the phenanthrazine was 0.1 g (25% of the theoretical).

Coupling the dye XI at a pH of 12.0-11.8 – synthesis of 1,5-disbenzeneazo-2,8-aminonaphthol-7-sulfo acid (XIV).

3.8 g of the dye (71% of the theoretical) was filtered out within 12 hours after coupling had begun.

6. Synthesis of 5-benzeneazo-2,8-aminonaphthol-7-sulfo acid (XIII).

Coupling the sulfo acid III at a pH of 12.0-11.8. The solution was filtered after 2 hours of coupling (no precipitate was found on the filter), and the dye, a finely crystalline dark powder, was precipitated from the filtrate by acidulating the latter with concentrated hydrochloric acid. The yield was 75-80% of the theoretical.

Attempt to synthesize a disazo dye from the dye XIII at a pH of 12.0-11.8.

After 3 hours of coupling the solution was filtered (no precipitate was found on the filter). A dye was precipitated from the filtrate by acidulating the latter with concentrated hydrochloric acid. The yield was 3 g (87.4% of the initial amount).

TABLE 3

Dye	Formula of dye	Weight, g	Temperature, °	Pressure, mm	Ml of N_2	Per cent N	
						Found	Computed
VII	$C_{16}H_{13}O_4N_3S$	0.1338	20	756	14.3	12.38	12.25
XI	$C_{16}H_{13}O_4N_3S$	0.2401	21	758	24.7	12.44	12.25
XIII	$C_{16}H_{13}O_4N_3S$	0.1160	20	766	12.4	12.5	12.25
XIV	$C_{22}H_{17}O_4N_5S$	0.1120	20	766	14.8	15.5	15.65

TABLE 4

Titration with Titanium Trichloride: Titer 0.0502

Dye	Formula of Dye	Weight, grams	$TiCl_3$ used in titration, ml	Molecular weight	
				Experimental	Computed
IX	$C_{16}H_{13}O_4N_3S$	0.01	3.9	318	343.2
X	$C_{22}H_{17}O_4N_5S$	0.1	6.1	405	447.4
XI	$C_{16}H_{13}O_4N_3S$	0.01	3.6	341	343.2

SUMMARY

1. It has been shown that the sulfo acids formed when 2,8-aminonaphthol is sulfonated with concentrated sulfuric acid at temperatures ranging from 0 to 30° are 2,8-aminonaphthol-5- and 7-sulfo acids.

TABLE 5

Molecular Weights, Calculated from the Data of Potentiometric Titration

($T_{HCl} = 0.003687$; $T_{NaOH} = 0.004577$)

Substance		Weight, g	Ml of HCl used to titrate one equivalent	Molecular weight	
				Experimental	Calculated
I	Sodium salt	0.1295	5.3	242.0	239.15
II		0.1250	4.5	272.0	261.15
III	....	0.1432	4.8	246.0	239.15
VII	Sodium salt	0.1650	4.6	352.0	365.14
IX		0.1852	5.5	330.0	347.2
XI		0.1852	5.3	350.0	343.2
XIII		0.2076	5.9	343.0	343.2

2. It has been found that 2,8-aminonaphthol-5- and 7-sulfo acids, in contrast to 2,8-aminonaphthol-6-sulfo acid (gamma acid), can form disazo dyes.

3. The experimental observations made in the present research fully confirm the predictions concerning the interaction of the sulfo acids of 2,8-aminonaphthol with diazo compounds based on the hypothesis we had advanced.

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* See CB translation p. 985 ff.

THE CHLOROMETHYLATION AND SUBSEQUENT REDUCTION OF AROMATIC NITRO COMPOUNDS

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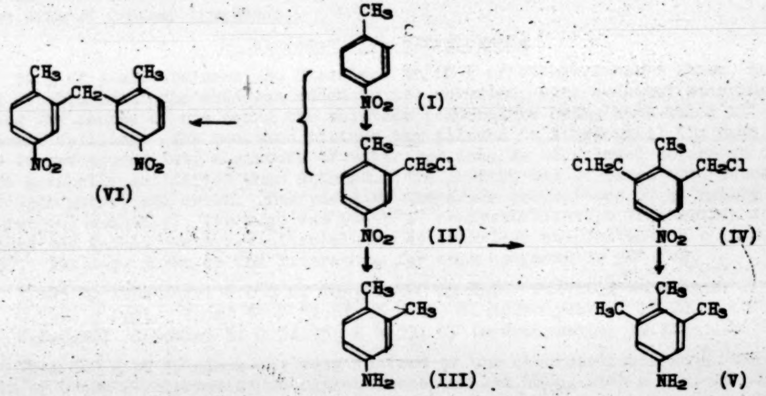
1,2,4-Xylidine (o-4-xylidine) is the principal initial product for the synthesis of Vitamin B_2 (riboflavin) [1]. We have pointed out previously [2] that the preparation of 1,2,4-xylidine from pure o-xylene by brominating and then aminating the latter was the most convenient method from the industrial point of view. But the production of pure o-xylene is a very difficult matter, since it requires the careful fractional distillation of the crude mixture of isomers and the freezing out of the o-xylene in special apparatus.

We chose a method of synthesizing 1,2,4-xylidine that involved the chloromethylation of p-nitrotoluene (I), followed by the reduction of the 2-chloromethyl-4-nitrotoluene (II) to 1,2,4-xylidine:



The chloromethylation of aromatic nitro compounds usually involves low yields [3]. We have shown that one chloromethyl group enters the aromatic nitro compound under relatively mild conditions, to wit: when the compound is reacted with dichloromethyl ether in the presence of chlorosulfonic acid or low-percentage oleum. 2-Chloromethyl-4-nitrotoluene is produced in a nearly quantitative yield under these conditions. We might have expected that the use of chlorosulfonic acid as the condensing agent would cause the chlorosulfonation of the nitro compound, but no reaction of this sort was observed at low temperatures. When the conditions were more severe – with 20-40% oleum or an excess of chlorofsulfonic acid present and a higher temperature (40-50°) – another chloromethyl group enters the p-nitrotoluene molecule, replacing the hydrogen atom at the 6 position (IV). We demonstrated the position of the second chloromethyl group by preparing the well-known 3,4,5-trimethylaniline (V) from the compound (IV) by reducing it.

When the chloromethylation was effected with 20% oleum, we noticed [3] the formation of a derivative of diphenylmethane (VI). We also secured this compound by using oleum to condense 2-chloromethyl-4-nitrotoluene with p-nitrotoluene; this also occurs as a side reaction in the chloromethylation of p-nitrotoluene.

The reduction of 2-chloromethyl-4-nitrotoluene to xylidine may be effected with tin and hydrochloric acid [3] or with hydrogen in acetic acid, using a platinum catalyst [4]. We hydrogenated 2-chloromethyl-4-nitrotoluene in an alcoholic alkaline medium with nickel, using highly diluted solutions at a pressure of 6-10 atm, the yield of 1,2,4-xylidine being 71% of the theoretical. When the solution concentration is higher or the amount of alkali is changed, hydrogenation follows a different course, and no amino compound is secured.

2-Chloromethyl-4-nitrotoluene has a highly toxic effect upon the skin; the addition of the second chloromethyl group to the nitro compound's molecule eliminates these toxic properties almost completely, however.

EXPERIMENTAL

Sym-Dichloromethyl ether was prepared with a yield of approximately 90% by reacting chlorosulfonic acid with paraformaldehyde; it was used for chloromethylation without further treatment.

2-Chloromethyl-4-nitrotoluene

50 g of p-nitrotoluene was dissolved in 60 g of dichloromethyl ether, and 85 g of chlorosulfonic acid was added to the solution, with constant stirring, during the course of one hour, the solution temperature being kept below 10° by external chilling. The reaction mixture was allowed to stand until the next day, when it was poured into a mixture of water and ice; an oily layer separated out, which gradually solidified when stirred. The product was filtered out, washed well with water, and dried. The yield of the crude product was 67 g (nearly the theoretical quantity); its m.p. was 54-56°. Recrystallization from methanol yielded the 2-chloromethyl-4-nitrotoluene as colorless needles with a m.p. of 61.5°. The m.p. given in the literature for this compound is 50° [3].

3.185 mg substance: 6.060 mg CO_2; 1.200 mg H_2O. 0.2710 g substance: 0.2106 g AgCl. Found %: C 51.88; H 4.21; Cl (hydrolyzable) 19.22. $C_8H_8O_2NCl$. Computed %: C 51.75; H 4.35; Cl (hydrolyzable) 19.11.

When 200 g of 5% oleum was used instead of the chlorosulfonic acid, the yield of crude 2-chloromethyl-4-nitrotoluene totaled 68 g, with a m.p. of 54-56°.

2,6-Bischloromethyl-4-nitrotoluene (IV)

10 g of p-nitrotoluene, 20 g of dichloromethyl ether, and 50 g of chlorosulfonic acid were stirred at 40-50° for two hours and then set aside to stand overnight. The further processing was like that set forth above. This yielded 15 g of a product, which was washed with a small amount of methanol and then recrystallized from benzene. The yield of 2,6-bischloromethyl-4-nitrotoluene was 5.2 g (30% of the theoretical), with a m.p. of 143-144°. The pure substance consisted of nearly colorless elongated prisms with a m.p. of 145°.

3.210 mg substance: 5.470 mg CO_2; 1.090 mg H_2O. 0.2692 g substance: 0.3305 g AgCl. Found %: C 46.47; H 3.77; Cl (hydrolyzable) 30.37. $C_9H_9O_2NCl_2$. Computed %: C 46.15; H 3.88; Cl (hydrolyzable) 30.38.

When 20% oleum was used, the yield of 2,6-bischloromethyl-4-nitrotoluene was 43% of the theoretical.

Reduction of 2,6-Bischloromethyl-4-nitrotoluene

1 g of 2,6-bischloromethyl-4-nitrotoluene was dissolved in 50 ml of glacial acetic acid and then hydrogenated by shaking with platinum catalysts; 5 mols of hydrogen were absorbed. The catalyst was filtered out of the resultant mixture, the acetic acid was driven off, ultimately with steam, and a sodium hydroxide solution was added to the residue left in the flask until its reaction was alkaline. 3,4,5-Trimethylaniline – colorless needles with a m.p. of 76-77° – was steam-distilled from the residue. The literature gives the m.p. of 3,4,5-trimethylaniline as 75° [5] or 79-80° [6].

Di-(2-methyl-5-nitrophenyl)-methane

9 g of 2-chloromethyl-4-nitrotoluene and 6.85 g of p-nitrotoluene were mixed with 35 g of 20% oleum. The next day the mixture was poured over ice, the resultant solid product being triturated in a mortar with water, filtered out, and dried (14.8 g). Washing the precipitate with methanol and recrystallizing it repeatedly from chloroform and benzene yielded di-(2-methyl-5-nitrophenyl)-methane as microcrystalline prisms with a m.p. of 155-157°.

3.050 mg substance: 7.045 mg CO_2; 1.300 mg H_2O. Found %: C 62.98; H 4.73. $C_{15}H_{14}O_4N_2$. Computed %: C 62.91; H 4.93.

1,2,4-Xylidine

6.77 g of pure 2-chloromethyl-4 nitrotoluenewas dissolved in 250 ml of anhydrous methanol; the solution was transferred to an autoclave, 4 ml of a 40% sodium hydroxide solution was added, and the whole was hydrogenated at a pressure of 6-10 atm for 45 minutes in the presence of pyrophoric nickel. When hydrogenation was complete, the catalyst was filtered out and washed with methanol, and the solvent was driven off from the acidulated solution, ultimately with steam. The solution that remained was alkalinized with sodium hydroxide, and the crystalline 1,2,4-xylidine steam distilled, the product filtered out, and more of the of the amino compound driven off from the mother liquor with steam. This yielded 3.1 g of 1,2,4-xylidine (71% of theory); colorless needles, m.p. 48-49°.

The crude 2-chloromethyl-4-nitrotoluene, prepared from 5 g of p-nitrotoluene, yielded 2.25 g of 1,2,4-xylidine, or 50% of the theoretical, based on the p-nitrotoluene.

Found %: N (Kjeldahl) 11.71. $C_8H_{11}N$. Computed %: N 11.57.

SUMMARY

It has been found that p-nitrotoluene is converted into 2-chloromethyl-4-nitrotoluene with a good yield by reacting it with dichloromethyl ether and chlorosulfonic acid or low-percentage oleum. When the reaction conditions are more severe, 2.6-bischloromethyl-4-nitrotoluene is formed. The mechanism of the side reaction resulting in the formation of di-(2-methyl-5-nitrophenyl)-methane has been established.

Hydrogenation of the resulting chloromethyl derivatives with platinum and nickel catalysts yields the corresponding amines.

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THE DIMETHYLAMIDATION OF CARBOXYLIC ACIDS

A. V. Kirsanov and Yu. M. Zolotov

It has recently been found that reacting sulfamide with carboxylic acids dissolved in pyridine produces high yields of amides of carboxylic acids [1]

We were interested in pursuing our research on this reaction, especially investigating the action of alkylated sulfamides on carboxylic acids, inasmuch as the resulting experimental data might shed light on the mechanism of the amidation reaction; moreover, the production of dialkyl amides from carboxylic acids directly is of even greater practical interest than the direct production of the unsubstituted amides.

If the intermediate reaction products are merely addition products of the carboxylic acids and sulfamide, amidation should involve the action of tetra-alkyl derivatives of sulfamide. But if the intermediate products are formed by the splitting off of ammonia or water, i.e., if the reaction requires 'free' hydrogen atoms in the sulfamide, the amidation reaction will not involve tetra-alkyl sulfamides.

Investigation of the action of carboxylic acids on as-dialkyl sulfamides is of particular interest, inasmuch as it is impossible to guess beforehand what the reaction will yield: a dialkyl amide, an unsubstituted amide, or a mixture of the two, while the results of studying this reaction would doubtless aid in explaining the mechanism of amidation.

The objective of the present paper is the study of the reaction of carboxylic acids with as-dimethylsulfamide; our investigation of the reactions with tri- and tetra-alkyl sulfamides will be described in one of our forthcoming papers.

It was found that as-dimethylsulfamide dissolved in pyridine reacts with carboxylic acids as readily as unsubstituted sulfamide does, the end products being nothing but dimethylamides of the carboxylic acids, with high yields, provided the reaction temperature does not exceed the boiling point of pyridine and heating is not continued for too long a time. The reaction is as follows:

$$RCOOH + NH_2SO_2N(CH_3)_2 \longrightarrow NH_2SO_2OH + RCON(CH_3)_2.$$

In one instance, after the reaction mixture had been boiled for a long time, a small quantity of the unsubstituted amide was formed, probably as the result of the following side reaction:

$$2NH_2SO_2N(CH_3)_2 \xrightarrow{+\ Py} NH(CH_3)_2 + NH_2SO_2NHSO_2N(CH_3)_2;$$

$$NH_2SO_2NHSO_2N(CH_3)_2 + RCOOH \rightarrow RCONH_2.$$

The fact that dimethylamine is evolved, rather than ammonia, when aqueous alkaline solutions are boiled corroborates this supposition.

The formation of dimethylamides from dimethylsulfamide and carboxylic acids proves that the sulfamide need only have two 'free' hydrogen atoms for the amidation reaction to take place; but we still do not know whether these two "free" hydrogen atoms are indispensable. The absence of unsubstituted amides among the reaction products under mild conditions may be due to the participation of these hydrogen atoms in the reaction mechanism, though the fact that only dimethylamides are formed is due to steric circumstances rather than to peculiarities of the reaction mechanism. Further tests are needed to provide a conclusive answer to this question.

Dimethylation with as-dimethylsulfamide was effected for the following acids: acetic (50% yield); phenylacetic (80%); benzoic (84%); ortho- and parachlorobenzoic (74 and 92%, respectively); and meta- and paranitrobenzoic acids (80 and 81%, respectively).

EXPERIMENTAL

Dimethylamidation of Acetic Acid

A mixture of 0.03 mole (1.72 ml) of acetic acid, 10 ml of anhydrous pyridine, and 0.03 mole (3.72 g) of dimethylsulfamide was heated with a reflux condenser over a boiling water bath. The transparent solution soon turned cloudy, and then a crystalline precipitate began to settle, which rapidly grew in size. Within two hours the reaction mixture was a thick paste of crystals impregnated with liquid. Heating was stopped after 3 hours; the pyridine was driven off at 30° in vacuum, and the residue was extracted 3 times with 30-ml batches of acetone. The acetone extracts were combined and the acetone was driven off over a water bath, leaving 2.6 g of an oily liquid as a residue. This liquid was distilled in a 4-mm vacuum. At 40-45°, 1.3 g of acetodimethylamide, or approximately 50% of the theoretical quantity, was distilled. The comparatively low yield was probably due to losses entrained with the pyridine and acetone vapors. The substance boiled at 162-164° at 748 mm. It had a n_D^{24} 1.4371 after distillation, which agrees with the data in the literature [2]. The acetodimethylamide was converted into the characteristic chloroaurate for more rigorous identification [2]. This was done by adding 0.087 g of the distilled acetodimethylamide to 0.3 g of auric chloride dissolved in 1 ml of 1 N hydrochloric acid. A yellow, sandy, crystalline precipitate was thrown down at once; it was suction-filtered out and washed with a small quantity of water. The yield was 0.22 g; the m.p. was 62-64°, with preliminary softening at 55°. It exhibited no depression when mixed with the known chloroaurate of acetodimethylamide.

0.1223 g substance: 0.0470 g Au. Found %: Au 38.40. $C_4H_9ON \cdot HAuCl_4 \cdot 5H_2O$. Computed %: Au 38.13.

All these results are in conformity with the data in the literature for acetodimethylamide [2].

Dimethylamidation of Phenylacetic Acid

A mixture of 0.0025 mole (0.34 g) of phenylacetic acid, 0.0025 mole (0.31 g) of dimethylsulfamide, and 3 ml of anhydrous pyridine was heated to 125° for 45 minutes over an oil bath. The pyridine was driven off in vacuum and 3 ml of a 10% soda solution was added to the dry residue; the mixture was again evaporated in vacuum, and the dry residue was twice extracted with 10-ml batches of acetone. The acetone was driven off over a water bath, and the residue was extracted 3 times with 10-ml batches of petroleum ether. The petroleum ether was driven off over a water bath; the residue was a nearly colorless oily liquid, which soon crystallized almost entirely. It was pressed out between sheets of filter paper, after which it consisted of colorless prisms, with a m.p. of 40-41.5°, which exhibited no depression when mixed with the known dimethylamide of phenylacetic acid [3]. The yield was 0.32 g, or about 80% of the theoretical.

Dimethylamidation of Benzoic Acid

This was carried out like the dimethylamidation of phenylacetic acid. A mixture of 0.0025 mole (0.31 g) of benzoic acid, 0.0025 mole (0.31 g) of dimethylsulfamide, and 3 ml of pyridine yielded 0.32 g of benzodimethylamide, i.e., approximately 84% of the theoretical quantity. Its m.p. was 40-41° after having been pressed between sheets of filter paper, and it exhibited no depression when mixed with known benzodimethylamide [4].

Dimethylamidation of o-Chlorobenzoic Acid

This was carried out as specified for benzoic acid above. 0.01 mole (1.57 g) of o-chlorobenzoic acid, 0.01 mole (1.24 g) of dimethylsulfamide, and 5 ml of pyridine yielded 1.38 g of o-chlorobenzodimethylamide, i.e., approximately 74% of the theoretical. Its m.p. was 11.5-12.5° after having been frozen out, and it exhibited no depression when mixed with known o-chlorobenzodimethylamide [5].

Dimethylamidation of p-Chlorobenzoic Acid

This was effected as for the ortho isomer, the quantities used being the same. The yield was 1.7 g, i.e., about 92% of the theoretical. Recrystallization from an ether-petroleum ether mixture yielded transparent colorless needles with a m.p. of 57-58°, which exhibited no depression when mixed with known p-chlorobenzodimethylamide, [6].

Dimethylamidation of m-Nitrobenzoic Acid

This was carried out similarly, but the dry residue left after the water had been driven off in vacuum was extracted with acetone alone. 0.005 mole (0.84 g) of m-nitrobenzoic acid, 0.005 mole (0.62 g) of dimethylsulfamide, and 5 ml of pyridine yielded 0.78 g of crude m-nitrobenzodimethylamide, i.e., about 80% of the theoretical yield. Recrystallization from petroleum ether yielded transparent colorless prisms, with a m.p. of 80-81°. Inasmuch as m-nitrobenzodimethylamide has not been described in the literature, the preparation that served as a standard of comparison was prepared from m-nitrobenzoyl chloride and an aqueous solution of dimethylamine. Transparent colorless prisms with a m.p. of 80-81° after recrystallization from petroleum ether, which exhibited no depression when mixed with the product prepared by dimethylamidating m-nitrobenzoic acid.

8.25 mg substance: 1.028 ml N_2 (19°, 757 mm). Found %: N 14.51. C
$C_9H_{10}O_3N_2$. Computed %: N 14.44.

Dimethylamidation of p-Nitrobenzoic Acid

A mixture of 0.005 mole (0.84 g) of p-nitrobenzoic acid, 0.005 mole (0.62 g) of dimethylsulfamide, and 5 ml of pyridine was heated for 3 hours over a boiling water bath, after which the pyridine was driven off at 30° in vacuum. 5 ml of a 10% soda solution was added to the dry residue, and the p-nitrobenzodimethylamide was suction filtered out, washed with water, and dried in vacuum. The yield was 0.79 g, or about 81% of the theoretical. Colorless crystals, with a m.p. of 97-98°, after recrystallization from water. Since p-nitrobenzodimethylamide has not been described in the literature, the preparation that served as a standard of comparison was prepared from p-nitrobenzoyl chloride and an aqueous solution of dimethylamine. Colorless needles, with a m.p. of 97-98° after recrystallization from water, that exhibited no depression when mixed with the product prepared by dimethylamidating p-nitrobenzoic acid.

8.38 g substance: 1.047 ml N_2 (19°, 756 mm). Found %: N 14.53.
$C_9H_{10}O_3N_2$. Computed %: N 14.44.

Boiling a mixture of 0.005 mole (0.84 g) of p-nitrobenzoic acid, 0.005 mole

(0.62 g) of dimethylsulfamide, and 5 ml of pyridine and treating the reaction product with petroleum ether yielded 0.03 g ofp-nitrobenzamide, m.p. 196-197°, which exhibited no depression when mixed with known p-nitrobenzamide [7].

Action of Aqueous Alkali Upon Dimethylsulfamide

0.01 mole (1.24 g) of dimethylsulfamide was dissolved in 20 ml of a 0.5 N sodium hydroxide solution and in the course of 10 minutes 10 ml of distillate was distilled from the solution into a receiver containing 15 ml of 1 N hydrochloric acid. The distillate was evaporated in vacuum to dryness, the residue consisting of 0.75 g of dimethylamine hydrochloride, i.e., about 93% of the theoretical yield. The product was hygroscopic and dissolved nearly completely in chloroform. For identification, we converted the product into N-p-nitrophenyl-N'-dimethylurea, with a m.p. of 218-219°, which exhibited no depression when mixed with known N-p-nitrophenyl-N-dimethylurea [8].

SUMMARY

1. It has been shown that the dimethylamides of carboxylic acids are prepared by reacting *as*-dimethylsulfamide with carboxylic acids in pyridine, the yields being satisfactory.

2. Some ideas are presented concerning the mechanism involved in the amidation of carboxylic acids.

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*See CB translation p. a-675 ff.

THE SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

IV. 3-KETO-6-METHYL-1,2,3,9,10,11-HEXAHYDROPHENANTHRENE

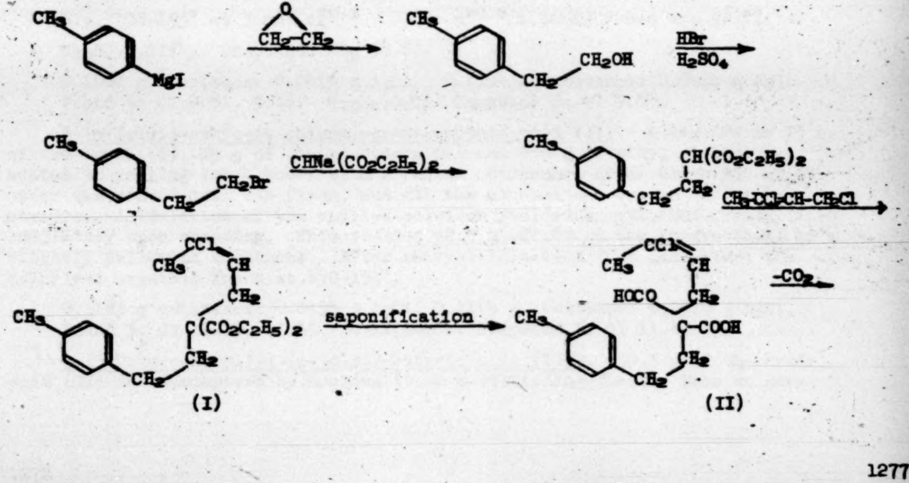
G. T. Tatevosyan and A. G. Vardanyan

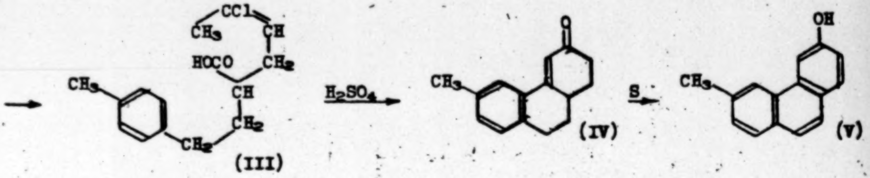
The most accessible keto derivatives of partially hydrogenated phenanthrene are the 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes. Owing to their ready availability, they have often been used in synthesizing analgesically active amino alcohols with the phenanthrene ring system [1], while the 7-methoxy derivative of 1-keto-1,2,3,4-tetrahydrophenanthrene has been utilized in numerous syntheses of hormone-active substances, chief of which have been the syntheses of the natural estrogenic hormones – equilenin [2] and estrone [3].

Very little research has been done, on the other hand, on ketones with the carbonyl group at the 2 or 3 positions, largely because of their rarity.

In our preceding reports [4], we showed that 3-keto-1,2,3,9,10,11-hexahydrophenanthrene and its homologs could be synthesized by reacting α-(3-chlorocrotyl)-γ-aryl butyric acids with sulfuric acid. Sulfuric acid hydrolyzes the former to δ-keto acids, the same reagent immediately causing a subsequent double cyclization. The initial α-(3-chlorocrotyl)-γ-aryl butyric acids are prepared by a malonic ester synthesis from the respective β-aryl ethyl bromides and 1,3-dichlorobutene-2, which is a waste product of one of the chemical industries.

The present paper describes the synthesis of one of these ketones – 3-keto-6-methyl-1,2,3-9,10,11-hexahydrophenanthrene (IV). The α-(3-chlorocrotyl)-γ-(p-tolyl)-butyric acid (III) used in this synthesis was prepared from p-iodotoluene as follows:


CH3
MgI
O
CH2–CH2
CH3
CH2OH
CH2
HBr
H2SO4
CH3
CH2Br
CH2
CHNa(CO2C2H5)2
CH3
CH(CO2C2H5)2
CH2
CH2
CH3–CCl=CH–CH2Cl
CCl
CH3
CH
CH2
CH3
C(CO2C2H5)2
CH2
CH2
(I)
saponification
CCl
CH3
CH
HOCO
CH2
CH3
C–COOH
CH2
CH2
(II)
–CO2



All the intermediate stages of this synthesis were carried through with high yields, so that the yield of the ketone (IV) was 54.5% of the theoretical based on the initial β-p-tolylethyl bromide.

When the ketone (IV) was heated with sulfuric acid, it was dehydrogenated readily and rapidly; this gave us a 61% yield of 3-hydroxy 6-methylphenanthrene (V), described for the first time.

EXPERIMENTAL

β-(p-Tolyl)-ethyl alcohol, prepared by reacting ethylene oxide with the magnesium derivative of p-iodotoluene [5], was converted into the corresponding bromide by reacting it with hydrobromic acid [6].

Condensing β-(p-tolyl)-ethyl bromide with sodium malonic ester yielded β-(p-tolyl)-ethyl malonate [7].

β-(p-Tolyl-ethyl-(γ-chlorocrotyl)-malonic ester (I).

75 g of freshly distilled 1,3-dichlorobutene-2 was gradually added, with constant stirring and water cooling, to a solution of the sodium derivative of β-(p-tolyl)-ethyl malonate, prepared from 153.5 g of that ester, 13 g of sodium and 240 ml of absolute alcohol. The mixture was boiled for 4 hours and then set aside to stand overnight. The next day most of the alcohol was driven off, and water acidulated with hydrochloric acid was added to the residue; benzene was used to separate the reaction product from the water, the benzene solution being washed with water and desiccated with sodium sulfate. The benzene was driven off, and the residue was distilled in vacuum. Double distillation yielded 174.4 g (86.2% of the theoretical) of a nearly colorless, thick liquid:

B.p. 192-195° at 3 mm; $d_4^{20.5}$ 1.0902; $n^{20.5}$ 1.5030; Found MR_D 99.37.

$C_{20}H_{27}O_4Cl\Gamma_4$. Computed: MR_D 98.67.

0.1082 g substance: 0.0416 g AgCl. 0.1194 g substance: 0.0468 g AgCl. Found %: Cl 9.51, 9.66. $C_{20}H_{27}O_4Cl$. Computed %: Cl 9.68.

β-(p-Tolyl)-ethyl-(γ-chloro)-crotylmalonic acid (II). A mixture of 75 g of the ester (I), 25 g of sodium hydroxide, and 350 g of ethyl alcohol was heated to boiling for 4 hours with a reflux condenser, after which 250 ml of water was poured into the flask, and all the alcohol was driven out of the mixture. Acidulation of the chilled solution yielded an oil that crystallized completely upon standing. This yielded 52.5 g (82.6% of the theoretical) of a slightly yellowish substance. After recrystallization from hot water, the colorless crystals fused at 150-151°.

0.1123 g substance: 0.0535 g AgCl. 0.1104 g substance: 0.0516 g AgCl. Found %: Cl 11.79, 11.56. $C_{16}H_{19}O_4Cl$. Computed %: Cl 11.43.

α-(3-Chlorocrotyl)-γ-(p-tolyl)-butyric acid (III). 39.7 g of the crude acid (II) was decomposed by heating it in a distilling flask. When no more carbon dioxide was evolved, the oil that remained was distilled in vacuum. This yielded 32.07 g (94% of the theoretical) of a slightly yellowish, extremely viscous oil:

B.p. 205-207° at 5 mm; d_4^{19} 1.1058; n_D^{19} 1.5298; MR_D Found 74.42; $C_{15}H_{19}O_2ClF_4$. Computed: MR_D 73.80.

0.1093 g substance: 0.0594 g AgCl; 0.1132 g substance: 0.0618 g AgCl. Found %: Cl 13.45, 13.51. $C_{15}H_{19}O_2Cl$. Computed %: Cl 13.54.

3-Keto-6-(methyl-1,2,3,9,10-11-hexahydrophenanthrene (IV). 182 ml of sulfuric acid (sp. gr. 1.80) was gradually added, with stirring, to 33 g of the acid (III), moderately cooled by water. The addition of the acid was accompanied by the evolution of large quantities of hydrogen chloride. The mixture was allowed to stand for half an hour at room temperature, and then it was heated to 60-75° for 4 hours over a water bath in an atmosphere of carbon dioxide, after which it was set aside to stand overnight. The next day the contents of the flask were poured over ice, and the resultant crystalline substance (after being allowed to stand for some time) was filtered out of the acid solution, washed with water, triturated in a mortar with an excess of a 10% sodium hydroxide solution, refiltered, washed, and dried. This yielded 21.4 g (81.5% of the theoretical) of a colorless substance. The colorless crystals of 3-keto-6-methyl-1,2,3,9,10,11-hexahydrophenanthrene had a m.p. of 104-105° after recrystallization from dilute alcohol.

0.1491 g substance: 0.4634 g CO_2; 0.1036 g H_2O; 0.1190 g substance: 0.3708 g CO_2; 0.0840 g H_2O. Found %: C 84.76, 84.98; H 7.72, 7.84. $C_{15}H_{16}O$. Computed %: C 84.90; H 7.55.

The orange-colored 2,4-dinitrophenylhydrazone, produced by allowing a mixture of 1.5 g of the ketone, 1.4 g of dinitrophenylhydrazine, and 200 ml of alcohol to stand at room temperature for 2 days, followed by boiling for half an hour, had a melting point of 231-232° after recrystallization from a chloroform-alcohol mixture.

0.1168 g substance: 15.4 ml N_2 (25°, 758 mm). Found %: N 14.73. $C_{20}H_{18}O_4N_4$. Computed %: N 14.81.

3-Hydroxy-6-methylphenanthrene (V). When 3 g of the ketone (IV) was heated to 180° with 0.9 g of sulfur, large quantities of hydrogen sulfide began to evolve. Dehydrogenation was continued for about one hour, until no more bubbles of hydrogen sulfide were given off, the temperature of the reaction mixture having been raised to 215° by the end of the reaction. The oil that was formed was poured into a porcelain dish while hot. The cooled product crystallized completely when it was rubbed with a glass rod. The substance was dissolved in 80 ml of a 10% sodium hydroxide solution, and the minute amounts of oil that remained undissolved were filtered out of the solution. Acidulating the filtrate precipitated a grayish-yellow crystalline substance. Triple recrystallization from dilute alcohol (boiling with charcoal) yielded the 3-hydroxy-6-methylphenanthrene as colorless acicular crystals, with a m.p. of 134-135°. The yield was 1.8 g (61.61% of the theoretical).

0.1037 g substance: 0.3276 g CO_2; 0.0555 g H_2O. 0.1002 g substance: 0.3177 g CO_2; 0.0546 g H_2O. Found %: C 86.16, 86.47; H 5.94, 6.05. $C_{15}H_{12}O$. Computed %: C86.54; H 5.77.

SUMMARY

1. 3-Keto-6-methyl-1,2,3,9,10,11-hexahydrophenanthrene has been synthesized by the sulfuric-acid hydrolysis and double cyclization of α-(3-chlorocrotyl)-γ-(p-tolyl)-butyric acid.

Dehydrogenation of the latter with sulfur yielded 3-hydroxy-6-methylphenanthrene.

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*See CB translation p. 289 ff.

THE CATALYTIC HYDROGENATION OF 2,7-DIMETHYLOCTADIYNE-3,5-DIOL-2,7

Yu. S. Zalkind* and L. F. Chelpanova

Not much work has been done on the addition of hydrogen to diacetylenic glycols in the presence of palladium or platinum.

It is asserted in the literature that with a platinum catalyst 8 atoms of hydrogen are added to 2,7-dimethyloctadiyne-3,5-diol-2,7 per molecule of the glycol [1].

A paper by Yu.S.Zalkind and I.Gverdtsiteli [2] reports that the hydrogenation of di-(1-hydroxycyclopentyl)-diacetylene with colloidal palladium slows down after four hydrogen atoms have been added. The authors did not investigate the hydrogenation products.

In his research on the hydrogenation of a diacetylene alcohol – 3-methyl-1,5-diphenylpentadiyne-1,4-diol with colloidal platinum, Yu.S.Zalkind [3] observed that this alcohol smoothly adds 8 hydrogen atoms to convert both of the triple bonds into single ones, forming a saturated alcohol; he also observed the formation of a saturated hydrocarbon as the result of the reduction of the hydroxyl group.

Yu.S.Zalkind and N.Iremadze [4] point out that when 2,7-di-p-tolyloctadiyne-3,5-diol-2,7 is hydrogenated with colloidal palladium, the reaction slows down suddenly as soon as four hydrogen atoms have been added, and the triple bonds have been converted into double ones, yielding a diethylenic glycol, i.e., hydrogenation of this glycol resembles the hydrogenation of an acetylenic glycol. When platinum is used for hydrogenation the reaction proceeds smoothly until eight atoms of hydrogen have been added.

In our research we had as our objective a study of the hydrogenation of 2,7-dimethyloctadiyne-3,5-diol-2,7 (I) and an analysis of its reduction products. The glycol was synthesized by condensing dimethylacetylenylcarbinol with cuprous chloride [1]. Recrystallization from aqueous alcohol yielded crystals with a m.p. of 132-133°, as stated in the literature.

The glycol was hydrogenated with colloidal palladium and platinum black. A series of hydrogenation tests with palladium demonstrated that this yielded a complex mixture of reaction products.

We found that, contrary to the assertions of Yu.S.Zalkind and N.Iremadze [4], the rate of hydrogenation exhibited no sharp break after four hydrogen atoms had been added, the reaction slowing down only after six atoms of hydrogen had been added. We therefore broke off hydrogenation after six atoms of hydrogen had been added per molecule of the diacetylenic glycol and investigated the resultant mixture of hydrogenation products.

We managed to isolate the following compounds from the mixture: a diethyllenic glycol – 2,7-dimethyloctadiene-3,5-diol-2,7 (II) – with a m.p. of 80-81° (approximately 25%, based on the original diacetylenic glycol); a diethylenic alcohol – 2,7-dimethyloctadien-4,6-ol-2 (III), with a b.p. of 76-78° at 4 mm (approximately 35-40%); the original 2,7-dimethyloctadiyne-3,5-diol-2,7 (I), with a m.p. of 132-133° (approximately 25%); and traces of a saturated glycol – 2,7-dimethyloctanediol-2,7 (IV), with a m.p. of 89-90°.

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*Deceased.

$$(CH_3)COH{-}C{\equiv}C{-}C{\equiv}C{-}COH(CH_3)_2;$$

(I)

$$(CH_3)_2COH{-}CH{=}CH{-}CH{=}CH{-}COH(CH_3)_2;$$

(II)

$$(CH_3)_2C{=}CH{-}CH{=}CH{-}CH_2{-}COH(CH_3)_2;$$

(III)

$$(CH_3)_2COH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COH(CH_3)_2.$$

(IV)

When hydrogenation is discontinued after four atoms of hydrogen have been added per molecule of the diacetylenic glycol, the same reduction products are secured, but their yields are lower, much of the original diacetylenic glycol being recovered unchanged.

When the diacetylenic glycol is hydrogenated with platinum black, eight hydrogen atoms are added evenly. Here again, we get a mixture of hydrogenation products, consisting chiefly of the saturated glycol (IV) (approximately 70%) plus an oily liquid (30%), containing the diethylenic alcohol (III) for the most part, with a slight admixture, most likely, of a saturated alcohol and minute traces of a saturated hydrocarbon. We made no investigation of the last two substances because of their minute quantities.

The original unreduced diacetylenic glycol (I) was crystallized out of the mixture of hydrogenation products, a fragrant yellow liquid, and was purified by repeated recrystallization from benzene. The diethylenic glycol $C_{10}H_{18}O_2$ (II) was recovered from the oily liquid by agitating the latter with water, in which it is rather freely soluble; the glycol had a m.p. of 80-81° after recrystallization.

The substance displayed unsaturated properties: it decolorized bromine water and an aqueous solution of potassium permanganate and absorbed four atoms of hydrogen when hydrogenated, being converted into the saturated glycol 2,7-dimethyloctanediol-2,7. The substance with a m.p. of 80-81° was oxidized to determine the position of its two double bonds.

The oxidation products: acetone, oxalic acid, and α-hydroxyisobutyric acid, indicated that this glycol was 2,7-dimethyloctadiene-3,5-diol-2,7 (II).

The oily substance secured after recovery of the glycol had a b.p. of 76-78° at 4 mm, and was identical with the diethylenic alcohol $C_{10}H_{18}O$ synthesized by A.I.Lebedeva by reducing 2,7-dimethyloctadiene-3,5-diol-2,7 electrolytically. The author comments that this yielded a mixture of products of varying degrees of hydrogenation, one of them being a fragrant substance with a b.p. of 73-75° at 3 mm [5],

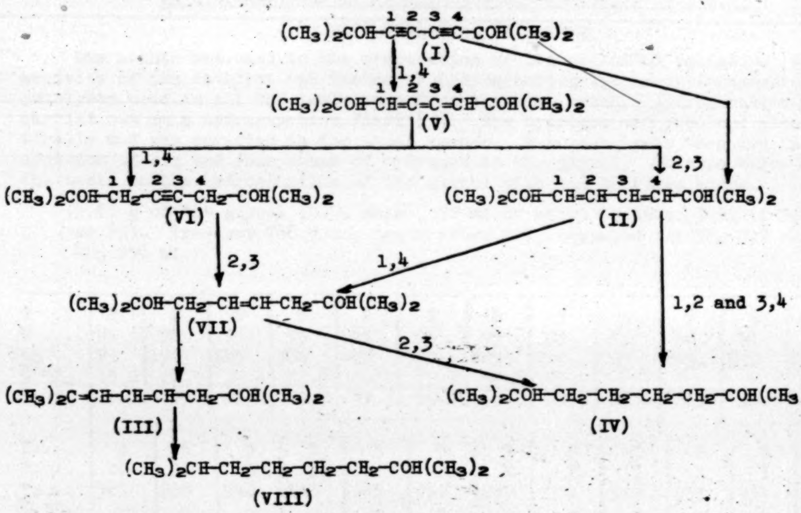
Analysis of this substance and of its oxidation products – β-hydroxyvaleric and oxalic acids and acetone – enabled A.I.Lebedeva to assign this substance the structure of 2,7-dimethyloctadien-4,6-ol-2.

The analysis and physical constants of our product with a b.p. of 76-78° at 4 mm agreed with A.I.Lebedeva's data. We therefore felt that we could dispense with its oxidation and forthwith call it 2,7-dimethyloctadien-4,6-ol-2 (III) as well.

The saturated glycol $C_{10}H_{22}O_2$ fused at 89-90°; its properties and analysis were those of 2,7-dimethyloctadiol-2,7 (IV) described in the literature.

The products of the reduction of 2,7-dimethyloctadiyne-3,5-diol-2,7 we have isolated enable us to outline the following hydrogenation for this diacetylenic glycol (Diagram I):

Diagram I


1 2 3 4
(CH3)2COH-C≡C-C≡C-COH(CH3)2
(I)
1,4
1 2 3 4
(CH3)2COH-CH=C=C=CH-COH(CH3)2
(V)
1,4
2,3
1 2 3 4
(CH3)2COH-CH2-C≡C-CH2-COH(CH3)2
(VI)
1 2 3 4
(CH3)2COH-CH=CH-CH=CH-COH(CH3)2
(II)
2,3
1,4
(CH3)2COH-CH2-CH=CH-CH2-COH(CH3)2
(VII)
1,2 and 3,4
2,3
(CH3)2C=CH-CH=CH-CH2-COH(CH3)2
(III)
(CH3)2COH-CH2-CH2-CH2-CH2-COH(CH3)2
(IV)
(CH3)2CH-CH2-CH2-CH2-CH2-COH(CH3)2
(VIII)

The original glycol (I) adds 4 hydrogen atoms at once, being converted into the diethylenic glycol (II), which is then reduced at the 1,4 position, forming the ethylenic glycol (VII). We were unable to isolate this substance , as it is quickly dehydrated, yielding a diethylenic alcohol (III).

Complete reduction of the diethylenic glycol (II) yields a saturated glycol (IV), while complete reduction of the diethylenic alcohol (III) yields a saturated alcohol (VIII).

In view of the fact that no break was observed in the rate of hydrogenation after four atoms of hydrogen had been added to the diacetylenic glycol (formation of the diethylenic glycol II), we could assume that the reduction of the diacetylenic glycol also followed a different course, involving the addition of hydrogen at the 1,4 position and the formation of the intermediate triene glycol (V), hydrogenation of which at the 1,4 position yields the acetylenic alcohol (VI), while hydrogenation at the 1,3 position yields the diethylenic glycol (II). The latter is then reduced to the ethylenic glycol (VII), which gives up water to form the diethylenic alcohol (III).

As has been stated above, we succeeded in isolating the diethylenic glycol (II), the diethylenic alcohol (III), and the saturated glycol (IV); hydrogenation with platinum also yielded a small amount of the saturated alcohol (VIII).

It is quite likely that the hydrogenation of 2,7-dimethyloctadiyn3-3,5-diol-2,7 takes place in several ways at once, resulting in a variegated mixture of products of various degrees of reduction. Further research is required to secure a complete picture of the hydrogenation process.

EXPERIMENTAL

I. Hydrogenation of 2,7-Dimethyloctadiyne-3,5-diol-2,7 with Colloidal Palladium

Gum arabic was used in the preparation of the colloidal palladium [6]; the activity of the catalyst was tested by hydrogenating tetramethylbutynediol. The catalysts used in all the tests came from the same batch. Hydrogenation was carried out in a hydrogenation flask [7]. The hydrogen was produced electrolytically and was purified in the usual manner. Numerous tests were run on the addition of six and four atoms of hydrogen to the glycol. We cite below one of the tests on the hydrogenation of the glycol with six hydrogen atoms.

1.66 g of the glycol (0.01 mole), 50 ml of ethyl acetate, 3 ml of Pd (3 mg Pd). Pressure 768.5 mm; temperature 20°; computed for $3H_2$ 717 ml, for $4H_2$ 956 ml.

T	2	2	2	2	2	2	2	3	5	5	5	5	5
V	95	95	95	95	95	95	95	95	43	40	25	25	20
v_0 ...	95	190	285	380	475	570	665	760	805	845	870	895	915
% $3H_2$.	13.2	26.4	39.6	52.8	66.0	79.2	92.6	105.9	–	–	–	–	–
% $4H_2$	9.9	19.0	29.7	39.7	49.7	59.7	69.7	79.5	84.1	88.9	90.9	93.5	95.7

T....	5	5	5	5	5	5	5	5	5	5	5	5	5
V....	10	10	5	3	2	2	2	2	1	1	1	1	1
v_0...	925	935	940	943	945	947	949	951	952	953	954	955	956
% $3H_2$	–	–	–	–	–	–	–	–	–	–	–	–	–
% $4H_2$	95.8	96.8	97.0	97.8	97.9	98.1	98.3	98.5	98.7	99.1	99.4	99.7	100

T is the time in minutes from the start of the run; V is the volume of hydrogen in milliliters absorbed in the time elapsed since the previous run; v_0 is the volume of hydrogen absorbed since the start of the run; $4H_2$ is the same volume expressed in per cent.

After the catalyst had been filtered out, the solution of reduction products was desiccated with sodium sulfate, and nearly all the ethyl acetate was driven off. This left a fragrant oily liquid, from which crystals settled out upon standing. The crystals were filtered out of the oily liquid, washed with petroleum ether, and recrystallized from benzene; they then had a m.p. of 132-133° and exhibited no depression of the melting point when mixed with the original glycol. The unreacted glycol averaged 25% of the original total.

After the crystals had been filtered out of the oily liquid, the latter was shaken vigorously with water several times. Driving off the water yielded a white crystalline substance, which was washed repeatedly with small batches of petroleum ether; its m.p. was 80-81° after several recrystallizations from benzene.

The yield was 25% of the original diacetylenic glycol.

A minute quantity of crystals with a m.p. of 89-90°, corresponding to the saturated glycol 2,7-dimethyloctanediol-2,7, was recovered from the mother liquor.

1. Analysis of the hydrogenation product with a m.p. of 80-81°.

0.0784 g substance: 0.2042 g CO_2; 0.0748 g H_2O. Found %: C 70.90; H 10.65. $C_{10}H_{18}O_2$. Computed %: C 70.58; H 10.59. 0.1119 g substance; 10.02 g C_6H_6: Δt 0.35°. Found: M 170.4. Computed: M 170.0.

Determination of the number of hydroxyl groups by the Terentyev method: 0.0222 g substance; 5.4 ml CH_4 (13°, 762 mm). Found: $\underline{v}_o$ 5.09; % OH 17.10. $C_{10}H_{16}(OH)_2$. Computed: $\underline{v}_o$ 5.85 ml; % OH 20.00.

The substance decolorizes bromine water and potassium permanganate.

Reduction of the substance with a m.p. of 80-81° with platinum black. We took 0.33 g of the substance, 20 ml of ethyl acetate, and 0.03 g of platinum black. 100 ml of hydrogen (760 mm) was added, 86.8 ml being called for theoretically for two double bonds. Filtering out the catalyst and driving off the solvent yielded a crystalline substance with a m.p. of 88-90°, which exhibited no depression of the melting point when mixed with the known saturated glycol.

Oxidation of the substance with a m.p. of 80-81°. After we had oxidized the substance with a 2% aqueous solution of potassium permanganate in the cold and separated the neutral and acid oxidation products in the usual manner, we found acetone in the neutral substances; the acetone displayed a positive reaction with sodium nitroprusside and formed a p-nitrophenylhydrazone with a m.p. of 149°.

The aqueous solution of the acid oxidation products contained oxalic acid, with a m.p. of 101-102°, identified by its insoluble potassium salt, and α-hydroxyisobutyric acid, with a m.p. of 78-79°.

Analysis of the silver salt:

0.0551 g salt; 0.0285 g Ag. Found %: Ag 51.72. $C_4H_3O_3Ag$. Computed %: Ag 50.95.

These results indicate that the substance with a m.p. of 80-81° is a diethylene glycol – 2,7-dimethyloctadiene-3,5-diol-2,7 (II).

2. Analysis of the oily substance with a b.p. of 76-78° at 4 mm.

After the unreacted diacetylenic glycol and the synthesized diethylenic glycol had been eliminated, the oily liquid was distilled in vacuum at 4 mm. The following three fractions were collected:

1) b.p. 38-70°, 12-15%; 2) b.p. 70-80°, 50-60%; 3) b.p. above 80° with decomposition, 25%.

The first and third fractions were not analyzed; several redistillations of Fraction 2 at reduced pressure yielded 7 g of a very fragrant, colorless oily liquid, with a b.p. of 76-78° at 4 mm, which decolorized bromine water and a potassium permanganate solution.

0.1018 g substance; 0.2898 g CO_2; 0.1089 g H_2O. Found %: C 77.64; H 11.77. $C_{10}H_{18}O$. Computed %: C 77.92; H 11.69. 0.0713 g substance; 13.00 g C_6H_6: Δt 0.18°. Found: M 153.6. $C_{10}H_{18}$. Computed: M 154.

Determination of the number of hydroxyl groups by the Terentyev method: 0.0436 g substance: 8.0 ml CH_4 (15°, 752 mm). Found: $\underline{v}_o$ 7.0 ml; % OH 12.2. $C_{10}H_{17}(OH)$. Computed: $\underline{v}_o$ 6.34 ml; % OH 11.0.

500 ml of hydrogen was absorbed during the catalytic reduction of 1.542 g of the substance with a b.p. of 76-78°, using 50 ml of ethyl acetate and 0.32 g of platinum black. Two double bonds require 492.3 ml of hydrogen (760 mm) theoretically.

These results enable us to call the substance with a b.p. of 76-78° at 4 mm a diethylenic alcohol – 2,7-dimethyloctadien-4,6-ol-2 (III).

II. Hydrogenation of 2,7-Dimethyloctadiyne 3,5-diol-2,7 With Platinum Black

The platinum black was prepared by the Loew method [8]. Several hydrogenation tests were made; we cited one of them below.

1.66 g of the glycol (0.01 mole), 50 ml of ethyl acetate, and 0.5 g of platinum black. Pressure 737 mm; temperature 17°; computed for $4H_2$ 1003 ml.

T	3	3	3	3	3	3	4	5	7	12
V	100	100	100	100	100	100	100	100	100	100
v_0	100	200	300	400	500	600	700	800	900	1000
% $4H_2$.	10	20	30	40	50	60	70	80	90	100

Eight atoms of hydrogen were added smoothly, after which the reaction slowed down considerably, so that hydrogenation was discontinued after eight hydrogen atoms had been added. The catalyst and the solvent were removed in the usual manner, and the hydrogenation products were analyzed.

Approximately 70% (based on the original glycol) of a crystalline substance with a m.p. of 88-90° and some 30% of an oily liquid were recovered.

1. Analysis of the hydrogenation product with a m.p. of 89-90°. The substance had a m.p. of 89-90° after recrystallization from petroleum ether and did not decolorize bromine water or potassium permanganate.

0.1082 g substance: 0.2756 g CO_2; 0.1238 g H_2O. 0.1040 g substance: 0.2618 g CO_2; 0.1161 g H_2O. Found %: C 69.08, 68.66; H 12.64, 12.40. $C_{10}H_{22}O_2$. Computed %: C 68.97; H 12.64.

Determination of the number of hydroxyl groups by the Terentyev method: 0.300 g substance: 8.5 ml CH_4 (16°, 740 mm). Found: v_0 7.5 ml; % OH 19.10. $C_{10}H_{20}(OH)_2$. Computed: v_0 7.6 ml; % OH 19.54.

These results indicated that the substance with a m.p. of 89-90° was a saturated glycol – 2,7-dimethyloctanediol-2,7 (IV).

2. Analysis of the oily liquid. After the crystals had been filtered out of the oily liquid, the latter was distilled in a 4-mm vacuum, the following three fractions being collected:

1) b.p. 65-70°, about 10-15%; 2) b.p. 70-90°, about 50%; 3) b.p. above 90°, with partial decomposition, about 20%.

Fraction 2 did not exhibit a sharp boiling point or precise analytical data even after repeated distillation; it reacted with bromine and with an aqueous potassium permanganate solution, contained hydroxyl groups, and most likely was a mixture of several substances. 5.8 g of this liquid was reacted with bromine in a carbon tetrachloride solution until the last drop of bromine was not decolorized. After the solvent had been driven off, the residue was distilled at 4-mm vacuum. Two fractions were collected: 1) b.p. 68-70°, about 50%; and 2) b.p. 98-100°, about 50%.

Fraction 1 contained no bromine, did not decolorize bromine or potassium permanganate, and gave a positive reaction for the hydroxyl group.

0.388 g substance; 16.00 g C_6H_6: Δt 0.78°. Found. M 156.4.
$C_{10}H_{22}O$. Computed: M 158.

Determination of the number of hydroxyl groups by the Terentyev method: 0.0898 g substance: 12 ml CH_4 (21°, 764 mm). Found: v_o 11.0 ml; % OH 8.85. $C_{10}H_{21}OH$. Computed: v_o 12.7 ml; % OH 10.76. Determination of the molecular refraction: d^{20}_{20} 0.8200; MR_D found 49.3; computed 49.9.

These results seemed to indicate that the fraction with a b.p. of 68-70° at 4 mm was a saturated alcohol – 2,7-dimethyloctanol-2 (VIII).

Fraction 2, with a b.p. of 98-100° at 4 mm, contained bromine and gave a positive qualitative reaction for hydroxyl; it was not investigated further. It is highly probable that it consisted of bromination products of the diethylenic alcohol.

SUMMARY

1. It has been found that, in contrast to the acetylenic glycols, hydrogenation of the diacetylenic glycol 2,7-dimethyloctadiyne-3,5-diol-2,7 with colloidal palladium does not involve any break in the rate of hydrogenation after four atoms of hydrogen have been added. The reaction slows down after six atoms of hydrogen have been added per molecule of the glycol.

2. In catalytic hydrogenation with platinum black eight atoms of hydrogen were added to the 2,7-dimethyloctadiyne-3,5-diol-2,7 smoothly.

3. The addition of six or eight atoms of hydrogen to the diacetylenic glycol with colloidal palladium yielded a mixture of products consisting of a diethylenic glycol (2,7-dimethyloctadiene-3,5-diol-2,7), a diethylenic alcohol (2,7-dimethyloctadien-4,6-ol-2), and the original diacetylenic glycol (2,7-dimethyloctadiyne-3,5-diol-2,7).

4. Hydrogenation of 2,7-dimethyloctadiyne-3,5-diol-2,7 with platinum likewise yielded a mixture, consisting of a saturated glycol (70%) and an oily substance (30%); the latter also was a mixture of diethylenic and saturated alcohols.

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ADDENDUM

After this paper had been submitted to the editors of the Journal of General Chemistry, one of its authors learned of a paper by I.M.Gverdtsiteli and S.G. Vashakidze, published in the Transactions of the J.V.Stalin State University of Tiflis (no. 36, 1949).

In this paper I.M.Gverdtsiteli and S.G.Vashakidze report that the hydrogenation of 2,7-dimethyloctadiyne-3,5-diol-2,7 in alcohol with colloidal palladium is like that of acetylenic glycols, i.e., there is a sharp break in the rate of hydrogenation after four hydrogen atoms have been added.

The authors assert that they secured a diethylenic glycol with a m.p. of 57°, for which they cite the empirical formula, the molecular weight determination, and the active hydrogen, without proving its structure.

We found no break in the rate of hydrogenation in repeated hydrogenations of 2,7-dimethyloctadiyne-3,5-diol-2,7 in ethyl acetate, and the diethylenic glycol - 2,7-dimethyloctadiene-3,5-diol-2,7 - fuses at 80-81°, according to our findings.

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